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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

THE ANALYTICAL APPLICATIONS OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 10. THE RELATIVE STABILITY OF THIOOXINATES, AND THE EFFECT OF COMPLEXING AGENTS ON THE INTERACTION OF THIOOXINE WITH CATIONS*

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8-Mercaptoquinoline (thiooxine) forms with many elements intensely colored inner-complex salts which are soluble in organic solvents, and which are suitable for the photometric determination of a number of elements [1, 2]. The present article is devoted to a description of the results of a study of the relative stability of thiooxinates, and their behavior toward the action of complexing agents.

The stability series of thiooxinates. The relative stability of metal thiooxinates was determined in parallel by three methods based on: 1) substitution reactions; 2) the rate of formation of the thiooxinates, and 3) the extractability limits of the thiooxinates.

1. A chloroform solution of a thiooxinate was shaken for 1-2 minutes with excess of an aqueous solution of a cation, and, from the change in color of the chloroform layer, an assessment was made of the substitution of one metal by another in the thiooxinate. In the case of thiooxinates which were insoluble in chloroform or other organic solvents, tests for the substitution of one cation by another were carried out by the action of an aqueous solution of a salt of the cation on a solid thiooxinate which had been freshly prepared and carefully washed.

2. A solution of thiooxine dihydrate in an amount insufficient for complete binding of one of the cations was introduced into a test tube containing a solution of two metals in equal molar concentrations. The thiooxinate formed was extracted with chloroform, and, from the color of the extract, conclusions were made regarding the metal thiooxinate formed.

Both experimental variants were carried out in the same hydrogen-ion concentration range within which the complex formed has the highest stability.

3. The relative stability of the complexes can also be established on the basis of the extractability ranges in acid and alkaline solutions [1, 2] determined previously.

The following series was established for the thiooxinates on the basis of the experiments carried out:

$$\mathrm{Re} > \mathrm{Au} > \mathrm{Ag} > \mathrm{Hg} > \mathrm{Pd} > \mathrm{Pt} > \mathrm{Ru} > \mathrm{Os} > \mathrm{Mo} > \mathrm{Cu} > \mathrm{W} > \mathrm{Cd} >$$
$$\mathrm{In} > \mathrm{Zn} > \mathrm{Fe} > \mathrm{Ir} > \mathrm{V} > \mathrm{Co} > \mathrm{Ni} > \mathrm{As} > \mathrm{Sb} > \mathrm{Sn} > \mathrm{Bi} > \mathrm{Pb} > \mathrm{Mn} > \mathrm{Tl}.$$

This practical stability series of the thiooxinates is only a guide, since the methods given above do not always give similar results. The accurate position of certain individual elements can only be established after determining the dissociation constants of the thiooxinates of these elements.

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*For communication 9, see Biokhimiya 23, 845 (1958). (See C.B. translation)

Pilipenko [3] established a similar stability series for xanthogenates:

$$Hg^{II} > Hg^{I} > Au > Ag > Cu > Bi > Pb > Cd > Ni > Fe > Zn.$$

He showed that the xanthogenate series does not correspond completely to the sulfide series established by Tananaev [4] on the basis of the work of Bruner and Zawadsky [5]:

$$Au_2S_3 > HgS > Ag_2S > CuS > Bi_2S_3 > CdS > PbS > NiS > ZnS < FeS.$$

Complete coincidence with the sulfide series can only be expected in the case of the salts of mercaptans, thiophenols, and other HS-reagents which are incapable of inner-complex formation, since it is generally known that the stability of inner-complex salts depends on the stability of both the electrovalent and the coordination bonds. This is very clearly demonstrated in the interaction of thiooxinates with hydrogen sulfide. The experiments were carried out as follows. A chloroform solution of a thiooxinate was shaken in a test tube with an aqueous solution of H_2S adjusted to pH 1, pH 3, and pH 10. A control test with water (without H_2S) was carried out at the same pH. It is clear from Table 1 that only the sulfides of seven elements (Ag, Hg, Sb, Pb, As, Bi, and Tl) are more stable than the thiooxinates. Hg, Ag, and As have an exceptionally high affinity for sulfur and form very stable sulfides. Sb, Pb, Bi, and Tl form less stable sulfides, and still less stable thiooxinates, in view of their incapacity to form stable coordination bonds with the nitrogen of the pyridine ring in thiooxine. Gold sulfide Au_2S_3 [6] is more stable than the sulfides of silver and mercury, but, in contrast to the thiooxinates of

TABLE 1

Interaction of H_2S with Thiooxinates

Thiooxinate	Reaction product of the thiooxinates with H_2S at various pH's		
	pH 1	pH 3	pH 10
Re	—	—	Na_2ReO_4 *
Au	—	—	—
Ag	Ag_2S	Ag_2S	Ag_2S
Hg	HgS	HgS	HgS
Pd	—	—	—
Pt	—	—	—
Ru	—	—	Partially decomposes
Os	—	—	—
Mo	—	—	—
Cu	—	—	—
W	—	—	Na_2WO_4 **
Cd	—	—	—
In	—	—	—
Zn	—	—	—
Fe	—	—	—
Ir	—	—	—
V	—	—	Decomposes***
Co	—	—	
Ni	—	—	—
As	As_2S_3	Forms slowly As_2S_3	Na_3AsO_3
Sb	Sb_2S_3	Sb_2S_3	Sb_2S_3
Pb	PbS	PbS	PbS
Sn	—	—	—
Bi	Bi_2S_3	Bi_2S_3	Bi_2S_3
Mn	Decomposes	Partially decomposes	—
Tl	Tl_2S	Tl_2S	Tl_2S
Ta	—	—	Decomposes
Nb	—	—	Decomposes

---

* Decomposes to perrhenate.

** Decomposes to tungstate.

*** Vanadate is formed in an alkaline medium in the presence of an oxidizing agent.

silver and mercury, gold thiooxinate is not decomposed by hydrogen sulfide because of the greater stability of the coordination bond Au ... N in this compound. Arsenic gives an exceptionally stable sulfide, but does not form a coordination bond at all with nitrogen, as a result of which arsenic thiooxinate is only stable in relatively weakly acid solutions. On the other hand, zinc forms a sulfide which is only relatively slightly stable, but, thanks to the capacity of zinc to form amines and coordination bonds with nitrogen, the thiooxinate of zinc is appreciably more stable than its sulfide. In general, the last members of the stability series of the thiooxinates, namely As, Sb, Sn, Bi, Pb, Mn, and Tl, do not form any sort of stable amines and coordination bonds with nitrogen, as a result of which their thiooxinates exhibit poor stability. Meanwhile, the stability of the thiooxinates in the series As, Sb, Sn, Bi, Pb, Mn, and Tl, in general, drops in the direction of a decrease in the stability of the sulfides. The last member of the series (the thiooxinate of univalent thallium) is appreciably hydrolyzed by water, and, in certain properties, already approximates the properties of the alkali metal thiooxinates.

Rhenium, palladium, gold, copper, silver, and mercury form stable sulfides, and, at the same time, form compounds with a stable coordination bond with nitrogen. Accordingly, their thiooxinates exhibit a high stability. This is in agreement with Kuznetsov's views [7]. In general, one has the impression that the sulfides are appreciably more stable than the mercaptides (salts of reagents of the type R-SH), when no inner complex formation occurs.

The Relative Stability of Oxinates and Thiooxinates

Thiooxine belongs to the class of reagents of type R-SH, while oxine belongs to the type R-OH. All the same, in connection with the similarity in the structure of the inner-complex salts formed by thiooxine and oxine, it was of interest to establish the relative stability of oxinates and thiooxinates in various media. For this purpose, a solution of an oxinate in chloroform was shaken with an aqueous solution of thiooxine at pH 1-2 and at pH 10. From the changes in the color of the chloroform layer, conclusions were then made regarding the relative stability of the oxinates or thiooxinates. In those cases where this experimental variant did not give decisive results or where the variant could not be carried out at all, excess of an alcoholic solution of a mixture of oxine and thiooxine in equimolar concentrations was added to an aqueous solution of the metal with a definite pH. The reaction product was extracted with chloroform, the color of which was then used to decide whether an oxinate or a thiooxinate had been formed. The results of these experiments are given in Table 2.

TABLE 2

Relative Stability of Oxinates and Thiooxinates at pH 1-2 and pH 10

Cation	pH 1 — 2		pH 10		Cation	pH 1—2		pH 10	
	oxinate	thiooxinate	oxinate	thiooxinate		oxinate	thiooxinate	oxinate	thiooxinate
Re	—	+	—	+	Fe	—	+	+	+
Au	—	+	—	+	Ir	—	+	—	+
Ag	—	+	—	+	V	+	—	—	—
Hg	—	+	—	+	Co	—	+	—	+
Pd	—	+	—	+	Ni	—	+	—	+
Pt	—	+	—	+	As	—	+	—	+
Ru	—	+	—	+	Sb	—	+	—	+
Os	—	+	—	+	Sn	—	+	—	+
Mo	—	—	—	—	Bi	—	+	—	+
Cu	—	+	—	+	Pb	—	+	—	+
W	—	—	—	—	Mn	—	+ (pH 6)	—	+
Cd	—	+	—	+	Tl	—	—	—	+
In	—	+	—	+	Ta *	—	+	+	—
Zn	—	+	—	+	Nb *	—	+	+	—

* Ta and Nb only react with thiooxine in strongly acid media at a high thiooxine concentration.

As is evident from Table 2, with the exception of vanadium (in acid media), and, presumably, tantalum and niobium (in alkaline media), the thiooxinates of all the other elements are more stable than the oxinates. In an alkaline medium the oxinate and thiooxinate of iron have, apparently, similar stability.

The Effect of Certain Masking Agents on the Interaction of Thiooxine with Cations

The stability of thiooxine salts depends to a very large extent on the concentration (excess) of thiooxine in solution, as a result of which the completeness of formation of the complexes can be controlled by changing the thiooxine concentration, and also by varying the acidity of the medium. Of essential importance is the fact that the stability of the thiooxinates of various elements changes to very different extents when the thiooxine concentration and the acidity of the solution are changed by the same amount. As shown in the work we have carried out, the reason for this appears to be the complexing action of hydrochloric acid (at sufficiently high concentrations), which is manifested to very different extents for the various elements.

Hydrochloric acid at high concentrations is a strong masking agent. This is particularly clearly shown in the following examples. As mentioned above, silver and mercury form very stable complexes with thiooxine, and, even in 30 N H_2SO_4, can be detected at a dilution of 1:50,000. At the same time, in 10 N HCl, mercury and silver are complexed into such stable complexes that they do not react with thiooxine even when the concentration of the latter is 10 mg/ml. Hydrochloric acid in sufficiently high concentrations will also complex iron, antimony, bismuth, cadmium, tin, and other elements. By increasing the HCl concentration it is possible to mask ever-increasing amounts of the elements mentioned above. For example, in 6 N HCl, it is possible to mask 80 mg of Fe^{3+} in a volume of 50 ml, and it would seem that it should be possible, by increasing the HCl concentration further, to mask even greater amounts of iron. However, quite unexpectedly, it was found that in 10 N HCl, iron, when only present in relatively small amounts (5-6 mg), passes into the chloroform extract in the form of a pale-yellow complex, when the normal thiooxinate of iron has an intensely red-brown color. It is obvious that in 10 N HCl, the chloride complex anions of iron $FeCl_4^-$ or $FeCl_6^{3-}$ become very stable, and, as a result of the formation of simple salts of these anions with thiooxine (e.g., $C_9H_6NSH \cdot H_3FeCl_6$), the iron is extracted with chloroform. That thiooxine is a component of the salts extracted is proved by the fact that, on shaking the extract with water or ammonia, the extract is colored an intense red-brown – as a result of the hydrolysis of the chloride complex and the formation of iron thiooxinate with a normal composition $Fe(C_9H_6NS)_2$.

Bi^{3+}, Sn^{IV}, As^{III} behave similarly at high hydrochloric acid concentrations (6-10 N); this usually leads to low results for the test element because of the saturation of the extractant with weakly colored salts formed between thiooxine and the chloride anions of the elements mentioned, this is particularly true when chloroform is the extractant. These complexes are only extracted to a weak extent by other solvents. The fact that appreciable amounts of thiooxine are complexed to give such complex compounds may also be responsible for the low results obtained. This is the case in 10 N HCl during the determination of rhenium in the presence of large amounts of molybdenum, tungsten, and tin (see [8]).

Thus, formation of stable chloride anions of the elements which complex thiooxine in a hydrochloric acid medium, can lead, in certain cases, to complications. Such phenomena are not observed in sulfuric acid media, but, in the latter, the selective action of thiooxine is appreciably less. On the other hand, the chloride ions of hydrochloric acid are capable of partially substituting hydrogen ions in such stable anions as molybdate, tungstate, perrhenate, and some others. As a result of the probable transfer during this process of the elements from an anionic to a cationic form, it becomes possible to realize a quantitative interaction of thiooxine with the elements mentioned in strongly acid solutions. For example, perrhenate ions interact quantitatively with thiooxine in 5-10 N HCl. At the same time, this reaction only proceeds partially in sulfuric acid, whatever the concentration of the latter.

Sodium fluoride is an outstanding masking agent for trivalent iron and quadrivalent tin in solutions which are not too acid. At pH 2-5 it is possible to mask 50-100 mg Fe^{3+} in a volume of 50 ml. At higher acidities, e.g., 0.5-2 N HCl, the fluoride complex of iron, as is well known, is unstable because of the competitive action of chloride ions. It would seem that masking of iron should not cease to be effective, but, nevertheless, in 2-2.5 N HCl (even in the presence of a large amount of fluoride), it is already difficult to mask 15-20 mg of iron. On increasing the HCl concentration further, the chloro complex becomes very stable, and in 6 N HCl it is possible to mask 80 mg of iron. The same is true of Sn^{IV}, the fluoride complex of which at high HCl concentrations changes into the chloride complex, which also does not react under these conditions with thiooxine. The other elements are not masked by sodium fluoride.

Thiourea efficiently masks Cu, Ag, Au, Hg, Os, Ru, and Pt in strongly acid solutions, but only weakly masks Pd. The efficiency of the action of thiourea increases with increasing acidity of the solution and increasing thiourea concentration. This is extremely important, since it masks the majority of the very elements which form the most stable thiooxinates. In relatively weakly acid solutions (e.g., at a pH of about 1) the masking action of thiourea is manifested to a very weak extent. In 6 N HCl, however, it is possible, in practice, to mask Cu, Os, and Ru in amounts of several mg, and to mask 50 mg of Hg, and about 10-20 mg of Ag, Au, and Pt. Antimony, bismuth, and other elements which form insufficiently stable thiourea complexes, are not masked by thiourea.

Potassium cyanide in alkaline solutions masks appreciable amounts of Fe, Cu, Ag, Au, Pt, Ru, Os, Ir, Ni, Co, Pd and Rh. Masking is carried out simply by adding excess KCN to weakly alkaline or ammoniacal solutions of the salts of the elements. Using such a technique, in a volume of 5 ml (plus 2 ml of 5% KCN) it is possible to mask 3 mg Ni, 50 mg Co, 20 mg Cu, 1 mg Pd, 10 mg Ir, 5-6 mg Os, Ru, and Pt, and 20-30 mg Ag and Au. Zinc, cadmium, and mercury are not masked by cyanide. The values given are only relative values, since the amount of the element masked depends on the KCN concentration of the solution. It is much more difficult to complex iron as a cyanide complex. The methods described in the literature for masking iron with cyanide[13] do not give the desired results when working with thiooxine, since, when such methods are used, the iron is only very incompletely converted into the hexacyanoferrate ion. We have found that by using ascorbic acid as a reducing agent, quantitative conversion of the iron cation into the hexacyanoferrate ion proceeds at a pH of not higher than 9-10. When such a technique is used, it is possible to mask 5 mg of Fe^{II} in 15-20 ml of solution.

Potassium thiocyanate in strong excess in an acid medium (pH 1-3) is a strong masking agent for trivalent iron. In the presence of thiooxine, when large amounts of iron are present, a crystalline raspberry-red precipitate is formed, which is insoluble in $CHCl_3$, CCl_4, and C_6H_6, and is soluble in isoamyl acetate and other esters. It is similar to compounds described in the literature, which are formed in the presence of Fe^{III}, thiocyanates, and heavy organic bases such as pyramidone [9], urotropine [10], acridine [11], or naphthylamine [12].

Cadmium and zinc at very high KSCN concentrations in solution (about 20%) do not react with thiooxine, but when high concentrations of Cd and Zn are involved, yellow crystalline precipitates separate out which are formed by the cation of thiooxine and the thiocyanate anions of zinc or cadmium. These precipitates, which are pale yellow in color, are soluble in chloroform. Mercury, antimony, bismuth, cobalt, the platinum metals, and other metals are not masked by potassium thiocyanate.

Potassium iodide masks bismuth and cadmium. When these elements are present in appreciable concentrations, crystalline precipitates formed between the iodide-complex anions and the thiooxine cation may separate out. Sb, Zn, and Hg, and other elements are not masked by iodide.

Phosphoric acid does not mask any of the test elements. Only a few tenths of a gram of trivalent iron can be masked by a concentrated solution of phosphoric acid.

Oxalic acid masks milligram amounts of divalent iron, tungsten, and vanadium. Other elements are not masked.

Ammonia does not firmly mask relatively small amounts of cobalt. Ammonia does not mask the remaining elements.

Tartaric acid in acid media masks moderate amounts of tungsten. Alkali solutions of tartaric and other hydroxy acids do not affect the interaction of thiooxine with other cations.

All that has been said relates to cases where a large excess of thiooxine is used in comparison with the concentration of the cations. When only a small excess of thiooxine is used, presumably, many weaker complexing agents will exhibit an appreciable masking effect.

SUMMARY

A stability series has been established for the thiooxinates of 26 elements. It has been shown that the stability of the thiooxinates depends not only on the bond metal—sulfur, but to a considerable extent on the stability of the bond metal—nitrogen.

In acid and alkali media, the thiooxinates of elements which form sulfides which are not hydrolyzed by water, are more stable than the oxinates, with the exception of those of vanadium (in acid solutions), and niobium and tantalum (in alkaline solutions).

When thiooxine is used for analytical purposes, the most powerful masking agents are: high concentrations of hydrochloric acid (for Fe, Mo, Hg, Ag, Bi, Sn, and Sb), thiourea (Cu, Ag, Au, Pt, Hg, Ru, and Os), and sodium fluoride (for Fe^{III} and Sn^{IV}), and, in alkaline solution, potassium cyanide (Fe^{2+}, Ag, Au, Pt, Ru, Os, Ir, Pd, Ni, and Co). Potassium thiocyanate is a good masking agent for Fe^{III} and moderate amounts of Zn and Cd.

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A POTENTIOMETRIC STUDY OF THE FORMATION OF MIXED URANYL AND ALKALI METAL FERROCYANIDES

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The reaction between uranyl salts and the ferrocyanides of the alkali metals has been known for a long time, but it has been studied to a comparatively small extent, although it is often used as a proof of the presence of uranyl ions in solution, the ferrocyanide used for this purpose being almost invariably potassium ferrocyanide. The published data on the composition of the precipitate formed thereby is contradictory. The question is complicated further by the fact that the composition of sparingly soluble ferrocyanides, as a number of workers have shown [1-3], depends on the nature of the univalent cations present in solution.

The published literature is devoted mainly to the composition of the uranyl ferrocyanide obtained on precipitating with potassium ferrocyanide; the following formulas, e.g., have been attributed to the compound thereby formed: $(UO_2)_2R$* [4]; K_2UO_2R [5]; $K_2UO_2R_xUO_2(NO_3)_2$, while in concentrated solutions there is a tendency for the following compounds to be formed: K_2UO_2R [6]; $K_4(UO_2)_4R_3$ [7, 3]; $K_{12}(UO_2)_8R_7$ is formed in the presence of excess K^+ ions [3].

There is less information on the composition of the uranyl ferrocyanide formed on precipitation with the ferrocyanides of the other alkali metals. The following formulas have been ascribed to the precipitates obtained with sodium ferrocyanide: $(UO_2)R_2$ [3]; $5(UO_2)_2R \cdot Na_4R$ and $5(UO_2)_2 \cdot R2Na_4R$** [8], while to the precipitates obtained with rubidium and cesium ferrocyanides the following formula has been ascribed: $M_4(UO_2)_4R_3$, where M = Rb, Cs [3].

Preparative methods and the solubility method have been used in the main in the papers cited; only individual results have been obtained by a potentiometric method. A study of the composition of the mixed ferrocyanides of copper [9] has, however, shown that the potentiometric method is fully applicable, and is very convenient for establishing the composition of mixed ferrocyanides, particularly in view of the fact that uranyl ferrocyanide is very easily peptized and leads to considerable difficulties when other research methods are used.

The present article is devoted to results obtained during a study of the interactions which occur in the system $UO_2^{2+}-M_4R-H_2O$, where M = Li, Na, K, Rb, and Cs.

The oxidation-reduction potential was determined on a LP-5 potentiometer using a platinum indicator electrode and a saturated calomel electrode.

Preliminary experiments were carried out on the potentiometric titration of solutions of uranyl nitrate with potassium ferrocyanide in order to establish the concentrations of the solutions, and the conditions under which the oxidation-reduction potential falls most sharply. It was established that only at comparatively high concentrations of the uranyl salt and of potassium ferrocyanide is there observed on the oxidation-reduction potential curves a characteristic break, which makes it possible to establish the composition of the mixed ferrocyanide of uranyl and alkali metal; sloping curves are obtained when low concentrations are used. A clearly defined break is obtained on introducing a comparatively large amount of ferrocyanide; preferably, the ferrocyanide should be added to the uranyl salt being titrated, rather than the other way around. The concentration of the working solutions of M_4R, M_3R, and $UO_2(NO_3)_2$ was about 0.1-0.2 mole/liter. During titration, 0.3 ml of ferrocyanide was

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*Here and henceforth R designates $[Fe(CN)_6]$.

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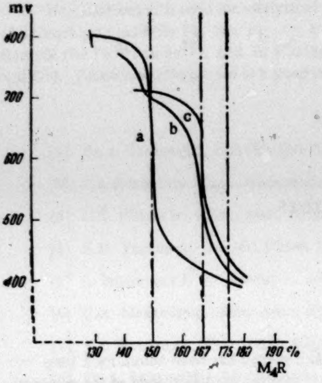


Fig. 1. Changes in the oxidation-reduction potential during titration of $UO_2(NO_3)_2$ with the following solutions: a) K_4R; b) K_4R + RbCl; c) K_4R + CsCl.

added to 10 ml of uranyl nitrate solution, and the volume of the solution made up to 50 ml. The solution was carefully agitated during titration.

In order to establish the relation between the composition of the precipitate and the nature of the alkali metal present in solution, the original solution of $UO_2(NO_3)_2$ was titrated with solutions of the ferrocyanides of potassium, sodium, and lithium, to which, in separate experiments, the following salts were added in equivalent amounts: RbCl or CsCl; KCl, RbCl, or CsCl; NaCl, KCl, RbCl, or CsCl. Twelve titrating solutions were thereby used.

Solutions of sodium and lithium ferrocyanides were prepared from potassium ferrocyanide via lead ferrocyanide [9]. Sodium and lithium ferricyanides were prepared by oxidation of the corresponding ferrocyanides with chlorine water.

On the basis of the experimental results obtained, diagrams were constructed in which the amount of the alkali metal ferrocyanide (expressed as a percentage of the amount necessary for forming normal uranyl ferrocyanide) was plotted along the abscissa, while the oxidation-reduction potentials were plotted along the ordinate.

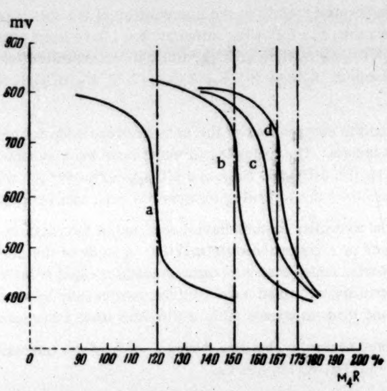


Fig. 2. Changes in the oxidation-reduction potential during titration of $UO_2(NO_3)_2$ with the following solutions: a) Na_4R; b) Na_4R + KCl; c) Na_4R + RbCl; d) Na_4R + CsCl.

The curves depicting changes in the oxidation-reduction potential during titration with potassium ferrocyanide are shown in Fig. 1. The most rapid drop in the oxidation-reduction potential is observed when, of the alkali metals, only potassium ions are present in solution, while the break in the curve is observed on addition of 149-150% of ferrocyanide (a). When titration is carried out with potassium ferrocyanide to which an equivalent amount of rubidium chloride has been added, the break on the curve (b) occurs at 167-168% ferrocyanide, while on addition of an equivalent amount of cesium chloride, the break occurs at 166-167% (c).

The change in oxidation-reduction potential during titration with sodium ferrocyanide is shown in Fig. 2. When only sodium ions are present, the break is observed on addition of 117-120% ferrocyanide (a). When titration is carried out with sodium ferrocyanide to which an equivalent amount of potassium chloride has been added, the break on the curve (b) is observed at 149-150%, i.e., on addition of the same amount of sodium ferrocyanide as in the titration with potassium ferrocyanide. When rubidium chloride (c) and cesium chloride (d) are added to the sodium ferrocyanide solution, the breaks on the curves are observed on addition of 164-165% and 166-167% of ferrocyanide.

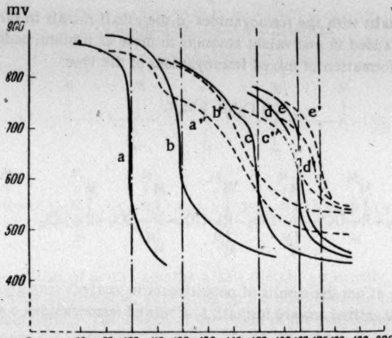
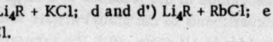


Fig. 3. Changes in the oxidation-reduction potential during titration of $UO_2(NO_3)_2$ with the following solutions: a) Li_4R; a') $Li_4R + LiCl$; b and b') $Li_4R + NaCl$; c and c') $Li_4R + KCl$; d and d') $Li_4R + RbCl$; e and e') $Li_4R + CsCl$.

The curves shown in Fig. 3 were constructed on the basis of the results obtained during titration with lithium ferrocyanide. When only lithium ions are present, the break on the oxidation-reduction potential curve (a) is observed on addition of 99-101% of ferrocyanide. During titration with lithium ferrocyanide in the presence of the ions of the other alkali metals, the same regularities are observed in the values of the oxidation-reduction potentials as during titration with sodium and potassium ferrocyanides. Thus, on titrating with lithium ferrocyanide solutions to which sodium chloride (b), potassium chloride (c), rubidium chloride (d), and cesium chloride (e) have been added in equivalent amounts, the breaks are observed on the curves at 118-120%, 149-150%, and 166-167% and 167-168% of ferrocyanide.

From the character of the curves for the oxidation-reduction potentials and the position of the breaks it can be concluded that during precipitation of uranyl salts with lithium ferrocyanide, normal uranyl ferrocyanide is formed: $(UO_2)_2R$.

During precipitation of the salts with sodium or lithium ferrocyanides in the presence of sodium ions introduced in an equivalent amount to the amount of lithium, presumably a mixed ferrocyanide of uranyl and sodium is formed $5(UO_2)_2R \cdot Na_4R$ or $Na_2(UO_2)_5R_3$. The structure of this salt can be depicted as follows:

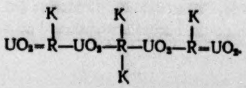


$$\mathrm{UO_2{=}\overset{Na}{\overset{|}{R}}{-}UO_2{-}\overset{UO_2}{\overset{\|}{R}}{-}UO_2{-}\overset{Na}{\overset{|}{R}}{=}UO_2}.$$

When potassium ferrocyanide, or lithium and sodium ferrocyanides in the presence of an equivalent amount of potassium, are added to a solution of an uranyl salt, then a mixed ferrocyanide of uranyl and potassium is formed

$$2(UO_2)_2R \cdot K_4R,$$

or, in another form

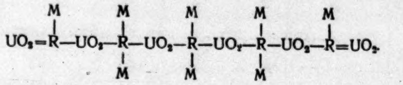


$$UO_2=\overset{K}{R}-UO_2-\overset{K}{\underset{K}{R}}-UO_2-\overset{K}{R}=UO_2.$$

During the interaction of uranyl salts with the ferrocyanides of the alkali metals in the presence of rubidium and cesium ions, when the latter are added in equivalent amounts to those of lithium, sodium, or potassium, the break on the curves corresponds to the formation of mixed ferrocyanides of the type

$$3(UO_2)_2R \cdot 2M_4R,$$

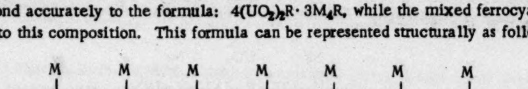
or, in another form



$$UO_2=\overset{M}{R}-UO_2-\overset{M}{\underset{M}{R}}-UO_2-\overset{M}{\underset{M}{R}}-UO_2-\overset{M}{\underset{M}{R}}-UO_2-\overset{M}{R}=UO_2.$$

Excess of alkali metal ions affect the results of potentiometric analysis strongly: the potential drop becomes less sharp, and the curve is shifted toward formation of mixed ferrocyanides containing a large amount of the alkali metals.

It should be pointed out that the shift in the break on the oxidation-reduction potential curve in the presence of excess alkali metal ions complicates the use of the potentiometric method for analytical purposes considerably. This is particularly clearly shown in Fig. 3, in which are shown the titration curves (a', b', c', d', and e') for uranyl nitrate with lithium ferrocyanide in the presence of a large excess of alkali metal ions. The alkali metal chlorides were added in these experiments to the uranyl nitrate solution in amounts such that the solutions were saturated with respect to the chlorides in all cases, with the exception of lithium chloride, which was added in an amount corresponding to a saturated solution of sodium chloride. It was established that, in the presence of large, excessive amounts of lithium, sodium, and potassium ions (a', b', and c') the oxidation-reduction potential curves do not exhibit sharp breaks, while,in the presence of rubidium and cesium ions (curves d' and e'), the break occurs at a point corresponding to 175% of ferrocyanide, the composition of the precipitates formed in this case corresponding to the formula: $4(UO_2)_2R \cdot 3M_4R$. It should be pointed out that, in this case, the volumes of the uranyl solutions containing excess rubidium and cesium that were taken were a tenth of those taken in other instances. Since the potentiometric titration curves obtained for solutions containing a large excess of Li^+, Na^+, and K^+, had a very sloping character without any clearly expressed breaks, determination of the compositions of the mixed uranyl ferrocyanides was carried out by titrating the excess of the alkali metal ferrocyanide with potassium permanganate in a strongly acid medium [10]. The ferrocyanides of K, Na, and Li were taken in amounts which were 3.5 times that theoretically required for the formation of normal uranyl ferrocyanide. The alkali metal chlorides were added in the amounts necessary for obtaining saturated solutions (apart from lithium chloride, which was taken in an amount corresponding to a saturated solution of sodium chloride). The mixed ferrocyanide of uranyl was then precipitated and the precipitate filtered off. Excess ferrocyanide in the filtrate was titrated with potassium permanganate. It was found that precipitates of the mixed ferrocyanides of uranyl with sodium and potassium correspond accurately to the formula: $4(UO_2)_2R \cdot 3M_4R$, while the mixed ferrocyanide of uranyl and lithium approximates to this composition. This formula can be represented structurally as follows:

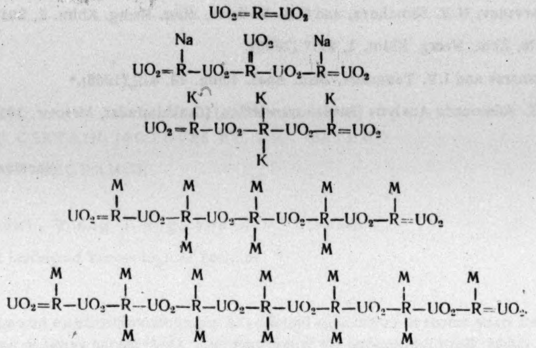


$$UO_2=\overset{M}{R}-UO_2-\overset{M}{\underset{M}{R}}-UO_2-\overset{M}{\underset{M}{R}}-UO_2-\overset{M}{\underset{M}{R}}-UO_2-\overset{M}{\underset{M}{R}}-UO_2-\overset{M}{\underset{M}{R}}-UO_2-\overset{M}{R}=UO_2.$$

The results obtained lead to the conclusion that the mixed ferrocyanides of uranyl and the alkali metals can be expressed by the general formula: $n(UO_2)_2 \cdot (n-1)M_4R$.

When M = Li, Na, K, Rb, and Cs, n assumes the values of 1, $1\frac{1}{4}$, 2, 3, and 3, respectively; in the presence of a large excess of Rb^+ and Cs^+, n = 4.

Structurally, the formulas can be represented as follows (M = Rb or Cs):



$$UO_2{=}R{=}UO_2$$

$$UO_2{=}\overset{Na}{R}{-}UO_2{-}\overset{UO_2}{\overset{\|}{R}}{-}UO_2{-}\overset{Na}{R}{=}UO_2$$

$$UO_2{=}\overset{K}{R}{-}UO_2{-}\overset{K}{\underset{K}{R}}{-}UO_2{-}\overset{K}{R}{=}UO_2$$

$$UO_2{=}\overset{M}{R}{-}UO_2{-}\overset{M}{\underset{M}{R}}{-}UO_2{-}\overset{M}{\underset{M}{R}}{-}UO_2{-}\overset{M}{\underset{M}{R}}{-}UO_2{-}\overset{M}{R}{=}UO_2$$

$$UO_2{=}\overset{M}{R}{-}UO_2{-}\overset{M}{\underset{M}{R}}{-}UO_2{-}\overset{M}{\underset{M}{R}}{-}UO_2{-}\overset{M}{\underset{M}{R}}{-}UO_2{-}\overset{M}{\underset{M}{R}}{-}UO_2{-}\overset{M}{\underset{M}{R}}{-}UO_2{-}\overset{M}{R}{=}UO_2.$$

Thus, the mixed ferrocyanides of uranyl and the alkali metals, apparently, are polymeric molecules in which the number of units can be appreciable, depending on the conditions (in particular, on the nature of the alkali metal present in the molecule). The length of the chain of the polymeric molecules, apparently, increases with the atomic weight of the alkali metal, and tends, in the limit, to the composition M_2UO_2R, but does not reach this composition even under very "severe" conditions (a large excess of alkali metal ions). In the polymeric molecules adduced, the alkali metals will probably undergo exchange (as in the case of ion exchange on resins) in order of increasing bond stability from Li to Cs.

SUMMARY

It has been established that the position of the equivalence point, corresponding to a break on the oxidation-reduction potential curves, in the systems $UO_2^{2+}-M_4[Fe(CN)_6]-H_2O$ (M = Li, Na, K, Rb, Cs) depends on the nature of the alkali metal present in solution. When lithium ferrocyanide is present, a normal uranyl ferrocyanide is formed $(UO_2)_2[Fe(CN)_6]$. When the remaining alkali metals are present, mixed ferrocyanides are formed:

$$Na_2(UO_2)_5[Fe(CN)_6]_3;\ 2(UO_2)_2[Fe(CN)_6]\,K_4[Fe(CN)_6];$$

$$3(UO_2)_2[Fe(CN)_6]\cdot 2Rb_4[Fe(CN)_6];\ 3(UO_2)_2[Fe(CN)_6]\cdot 2Cs_4[Fe(CN)_6].$$

In the presence of excess alkali metal ions the equivalence point is shifted toward formation of compounds containing large amounts of the alkali metals, while in the presence of very high concentrations of the solutions of alkali metal chlorides, a mixed uranyl ferrocyanide is formed:

$$4(UO_2)_2[Fe(CN)_6]\cdot 3M_4[Fe(CN)_6].$$

It is suggested that the mixed uranyl ferrocyanides be regarded as polynuclear molecules of the polymer type.

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SEPARATION OF CERTAIN ISOTOPES BY THE METHOD OF FOCUSING ION EXCHANGE

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Chromatography and electrochromatography have found application in recent years for separating fragments arising from the fission of heavy nuclei [1-4]. The duration of the experiment itself, which amounts to several hours, is a drawback of these methods. Of considerable interest is the search for new, more efficient methods of separation. Recently, a number of authors have suggested a new technique of electrophoretic separation of complex systems, in which a pH gradient, or a gradient in the concentration of complexing agents, is applied in parallel to the electric field. This technique has been used for separating both organic materials [5, 6] as well as inorganic ions [7-9]. The work described in the present article was carried out with the aim of studying the possibilities of using the method of focusing ion exchange for separating fission nucleides. We thought it would be of the greatest interest to follow the behavior of the rare earths, and to develop conditions for separating them from each other and from the alkaline earth elements.

The so-called method of focusing ion exchange has been described in a series of articles [5-9]. In a solution of a complexing agent which is capable of forming negatively charged ions with the ions of some elements, a mobile equilibrium is established between the various ionic forms. Let us imagine an extended (drawn out) capillary system, e.g., a sheet of filter paper in which, as a result of the transfer of the ions of a complexing agent in an electric field, a concentration gradient is established for this complexing agent. In such a case, in the region where there is a high concentration of the complexing agent, the negatively charged complex ions will predominate, while in the regions of low complexing agent concentration the cationic forms M^{n+} (Fig. 1) will dominate.

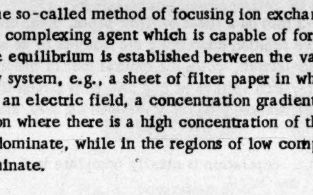

Fig. 1. Distribution of the ionic forms of an element M when a concentration gradient has been established for the complexing agent.

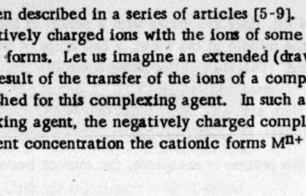

Fig. 2. Focusing process.

Under the action of an electric field, the negatively charged ions will move toward the anode, while the positively charged ions will move toward the cathode (Fig. 2).

As a result of this process, all the element M will be concentrated in a narrow zone. The position of this zone will be determined by the concentration gradient of the complexing agent, and also by the instability constant of the complexed ion.

If a mixture should contain several elements M_1, M_2, M_i, which give different complex compounds with the same complexing agent, and the instability constants of the complex anions formed are different, then a state of exchange equilibrium will be established between them. It is obvious that each of these elements will be concentrated in different places in accordance with their instability constants. Thus, it is possible that not only concentration will occur, but also separation of these elements.

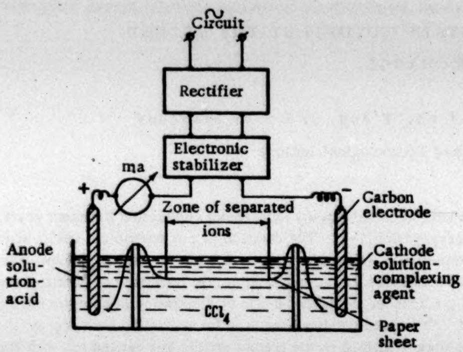

Fig. 3. Schematic diagram of the setup used for the separation.

The experimental setup is shown in Fig. 3.

First of all, lines are drawn with a pencil at intervals of 2-3 mm on a sheet of filter paper, then, on a certain part in the middle of the sheet, a few drops of the radioactive solution containing the isotopes to be separated is placed. The ends of the paper sheet dip into the electrode vessels, while the central part of the sheet is immersed in a vessel containing CCl_4. A current of 2-10 milliamp at a voltage of 260-280 volts (about 20-30 volts/cm) is then applied. In approximately 2-5 minutes, a concentration gradient is established, and, after another 2-3 minutes, the elements are separated and concentrated.

When the process is complete, the current becomes constant. Separation is usually complete in 5-10 min.

TABLE 1

Expt. No.	Cathode solution		Anode solution — hydrochloric acid	
	complexing agent	concentration complexing agent, M	pH	concentration *M*
1a	Sodium ethylene-diamine-tetracetate	0,1	11	0,5
1б		0,01	11	0,5
2a	» »	0,1	11	0,5
2б	» »	0,1	11	0,1
2в	» »	0,1	11	0,02
3a	» »	0,1	11	0,5
3б	» »	0.1	7	0,5
3в	» »	0,1	4	0,5
4a	» »	0,1	7	0,5
4б	Citric acid	0,03	12	0,5

The position of the zones is found either by means of autoradiography, or directly, by measuring the activity of parts of the paper and mapping out the activity distribution.

The separated isotopes are identified from the half-life period or by determining the maximum energy of the β-radiation.

Separation of Sr and Y. The separation of Sr^{90} and Y^{90} without carriers was studied first. Solutions of citric acid and sodium ethylenediaminetetracetate were used as complexing agents.

The experimental conditions are given in Table 1.

Changing the concentration of sodium ethylenediaminetetracetate in the cathode solution from 0.1 to 0.01 M affects separation of Sr^{90} and Y^{90} insignificantly. Lowering the concentration of sodium ethylenediaminetetracetate to 0.01 M leads to poorer separation; however, the separation is still complete. Variations in the pH of the electrode solutions also have little effect on the separation of the given isotopes.

Compared with sodium ethylenediaminetetracetate, citric acid (under the given experimental conditions) gave poorer results, however, here again complete separation of Sr^{90} and Y^{90} was achieved (Fig. 4).

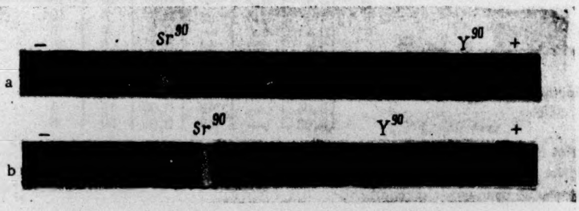

Fig. 4. Autoradiograph of the separation of Sr^{90} and Y^{90}: a) 0.1 M sodium ethylenediaminetetracetate; b) 0.03 M citric acid.

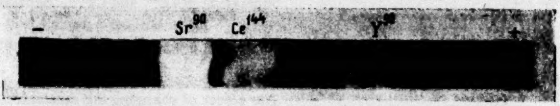

Fig. 5. Separation of Sr^{90}, Y^{90}, and Ce^{144}. Cathode solution – 0.03 M citric acid, pH 12; anode solution – 0.5 M HCl.

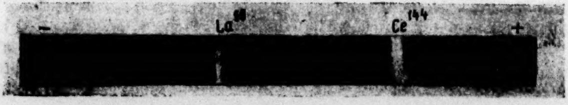

Fig. 6. Separation of La^{140} and Ce^{144} using a 0.5 M solution of sodium ethylenediaminetetracetate.

Separation of Sr^{90}, Y^{90}, and Ce^{144}. In the succeeding experiments, the possibility was established of separating Sr^{90}, Y^{90}, and Ce^{144} without introducing carriers. As in the previous series of experiments, citric acid and sodium ethylenediaminetetracetate were used.

The experimental conditions used, and the results obtained are given in Table 2.

The results given in Table 2 show that, as a rule, the distance between the zones for Ce^{144} and Y^{90} in citric acid are significantly greater than in sodium ethylenediaminetetracetate solutions.

TABLE 2

Cathode solution				Anode solution	Distance between the zones, mm	
Complexing agent	Concentration complexing agent, M	NaOH concentration, M	pH	HCl concentration, M	Sr and Ce	Ce and Y
Citric acid	0,01	***	12	0,5	30	45
" "	0,03	—	12	0,5	15	27
" "	0,05	—	12	0,5	8	20
" "	0,1	—	12	0,5	6	10
" "	0,5	—	12	0,5	0	4
" "	0,1*	0	—	0,5	—	—
" "	0,1	0,1	—	0,5	15	25
" "	0,1	0,3	—	0,5	10	20
" "	0,1	0,5	—	0,5	10	15
" "	0,1	0,8	—	0,5	6	10
" "	0,1**	1,0	—	0,5	0	0
" "	0,1	***	12	0,1	8	30
" "	0,1	—	12	0,3	8	16
" "	0,1	—	12	0,5	6	10
Sodium ethylenediaminetetracetate	0,1	***	9	0,03	12	4
	0,04	—	9	0,03	15	4
" "	0,02	—	9	0,03	30	6

*Not focused.

**Not separated.

***NaOH concentration constant.

In Fig. 5 is shown an autoradiograph of a paper sheet on which Sr^{90}, Y^{90}, and Ce^{144} have been separated in citric acid.

Separation of La^{140} and Ce^{144}. Separation of La^{140} and trivalent Ce^{144}, taken without a carrier, was carried out as before by means of sodium ethylenediaminetetracetate and citric acid.

The effect of changing the concentration of sodium ethylenediaminetetracetate from 0.01 to 0.1 M in the cathode solution was studied. It was found that separation of La^{140} and Ce^{144} occurred only when the sodium ethylenediaminetetracetate concentration was 0.5 M. As can be seen from the autoradiograph (Fig. 6), the distance between the zones in this case was 35 mm.

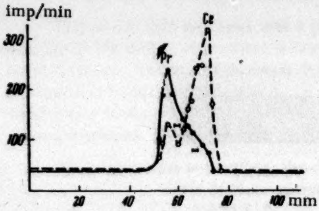

Fig. 7. Separation of Ce and P. Cathode solution – 0.025 M sodium ethylenediaminetetracetate, 0.025 M citric acid, pH 8; anode solution – 0.1 M HCl.

Separation of Ce and Pr. Separation of a mixture of cerium (III) and praseodymium in concentrations up to 0.5 mg/ml was studied in another series of tests. Ce^{144} and Pr^{144} (T = 17.5 minutes) were used as radioactive indicators.

Complete separation of Ce and Pr was not achieved on using sodium ethylenediaminetetracetate. A mixture of sodium ethylenediaminetetracetate and citric acid (Fig. 7) gives the best results.

SUMMARY

A study has been made of the possibility of separating Sr^{90}–Y^{90}, Sr^{90}–Y^{90}–Ce^{144}, and Ce^{144}–La^{140}, all taken without carriers, as well as the possibility of separating a mixture of Ce–Pr, by the method of focusing ion exchange. It has been established that mixtures of Sr^{90}–Y^{90}, Sr^{90}–Y^{90}–Ce^{144}, and Ce^{144}–La^{140} can be separated in the course of five minutes when citric acid or sodium ethylenediaminetetracetate are used; separation of a mixture of Ce–Pr in concentrations up to 0.5 mg/ml is not complete.

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HYDRON II – A NEW INDICATOR FOR THE COMPLEXONOMETRIC DETERMINATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM

I.S. Mustafin and E.S. Kruchkova

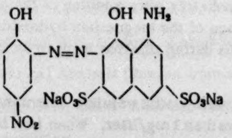
A number of indicators have been fairly successfully used for the complexonometric determination of total calcium and magnesium; they include: eriochrome black [1], acid chrome dark-blue, and acid chrome-blue K [2]; relatively recently some new, interesting indicator materials have been described [3, 4]. When one talks about the determination of one of the elements mentioned in the presence of the other, it should be borne in mind that an indicator cannot be found which will permit determination of magnesium in the presence of calcium, since sodium ethylenediaminetetracetate forms a less stable compound with magnesium than with calcium; the pH's of these complexes are, respectively, 8.69 and 10.59 [5].

Murexide is widely used as a complexonometric indicator for calcium in the presence of magnesium [6]; in the presence of magnesium, the change in the color of the solution being titrated from rose to lilac-violet at the end point is not sufficiently clear. Welcher [7] correctly notes that such an indicator change is far from complete.

New indicators have now been found which will permit complexonometric determination of calcium in the presence of magnesium. Calcion IREA [8], in particular, is such an indicator. This indicator gives a more contrasting color change at the end-point (from bright rose to blue) than murexide. The essential drawback of this indicator, however, is the high salt error, and the impossibility of determining calcium in the presence of appreciable amounts of magnesium.

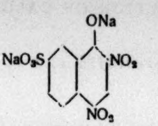
Lake red [9] exhibits a very small contrast in color change, and is not characterized by high sensitivity (5-10 μg/ml Ca^{2+}). It has been established that it is possible to use acid chrome dark-blue and acid chrome-blue as indicators for the complexonometric titration of calcium in the presence of magnesium in an alkaline medium [10]. The indicator change is characterized by a change in color from red to lilac-blue. Diehl and Ellingbone [11] recommend calcein, which is a condensation product of iminodiacetic acid with fluorescein; the indicator change is not characterized by a contrasting change in color (from yellow-green to brown). Worthy of attention as indicators are the azo compounds: 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid [12] and 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid [13]. When calcium is titrated with a solution of sodium ethylenediaminetetracetate using these indicators there is a color change from red to blue. Unfortunately, we did not have these indicators at our disposal.

During a systematic study of the analytical possibilities of hydroxyazo compounds, we found materials which, in alkaline media, interact with calcium and are indifferent to magnesium. Of these, the most interesting compound proved to be the dye, acid chrome dark-green Zh:



This material is a dark-brown powder which is readily soluble in water, but less soluble in alcohol; it is insoluble in benzene, chloroform, and dioxane. An alkaline solution of the dye (pH 12.5) has a violet-blue color; in the presence of calcium ions a bright-red color develops. The reaction sensitivity is 0.5 μg/ml Ca^{2+}. Under these conditions, the dye does not interact with magnesium, but its solution acquires a deeper blue shade.

When this dye is used as an indicator, the bright-rose color of the solution being titrated (excess Ca^{2+}) changes to violet-blue (excess sodium ethylenediaminetetracetate). Of course, such a change does not possess sufficient contrast; accordingly, we decided to mix the indicator material with a suitable inert dye. The latter, being an internal light filter, should be capable of enhancing the contrast in the color change of the indicator. Some authors [14-16] have tried in this way to increase the contrast in the color change of murexide. The same approach was also tried by Kuznetsov [9] for improving the indicator change of lake red.

For a number of reasons we chose, as the inert dye, naphthol yellow:  aqueous solutions of which have a yellow color, the color being independent of the pH.

We have designated the mixed indicator consisting of acid chrome dark-green Zh and the internal light filter – naphthol yellow – "Hydron II." On titrating calcium with a solution of sodium ethylenediaminetetracetate in an alkaline medium (2 ml of 1 N NaOH to 50 ml of solution being titrated), using Hydron II as indicator, the color changes from bright rose to green. Hydron II exhibits a slightly higher sensitivity toward calcium than the original dye (0.1 μg/ml Ca^{2+}) as a result of the increase in contrast of the final colors.

We have studied the possibility of the complexonometric determination of calcium in the presence of various amounts of magnesium. Titration was carried out with 0.02 N sodium ethylenediaminetetracetate in the presence of 2 ml of 1 N NaOH per 50 ml of solution until there was a change from a rose color to green; usually during the titration a precipitate of magnesium hydroxide separates out.

TABLE 1

Titration of Calcium in the Presence of Magnesium

Ca^{2+} taken, mg	Molar ratio of Ca : Mg	Ca^{2+} found, mg
3.246	1:0	3.246
3.246	1:0.1	3.253
3.246	1:1	3.253
3.246	1:10	3.258
0.324	1:100	0.327

The results given in Table 1 indicate that Hydron II permits fully satisfactory results to be obtained for the determination of calcium in the presence of 100 times its amount of magnesium.

In an alkaline medium magnesium does not interact at all with the indicator. However, when large amounts of magnesium are present in the solution being titrated, copious precipitation of magnesium hydroxide occurs, and the adsorption processes which accompany this precipitation complicate establishment of the end point; in such cases, it is necessary to dilute the solution more.

Titration should be carried out immediately after addition of the alkali, otherwise, on standing, the adsorption processes which occur on the surface of the magnesium hydroxide intensify and the indicator change deteriorates. Careful agitation of the solution during titration leads to an increase in the sharpness of the color change at the equivalence point.

Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, and Mn^{2+} interfere with calcium determination when Hydron II is used as indicator. Iron does not interfere at concentrations less than 1 mg/liter. When iron is present in larger amounts it depresses the results. When more than 200 mg/liter of iron is present titration of calcium becomes impossible because of the copious deposition of the brown hydroxide.

The presence of 20 mg of Al^{3+} per liter of test solution does not affect the titration results of any amount of calcium; when larger amounts of aluminum are present, the results obtained are somewhat low.

Hydron II has an insignificant salt error and permits titration of calcium in 10% NaCl solution, although, under such conditions, the contrast in the color change diminishes somewhat.

TABLE 2

Determination of the Calcium Hardness of Water Using Hydron II as Indicator

Test water	Hardness, mg · equiv/liter
Tap water	2.2302
Tap water diluted 10 times	0.2212
Tap water diluted 100 times	0.0228
Tap water diluted 500 times	0.0054

The results given in Table 2 indicate that Hydron II permits satisfactory determination of the calcium hardness of water with a low mineral content (5 μg-equiv/liter).

In order to determine the calcium hardness, 2 ml of 1 N NaOH is added to 50 ml of test water, followed by four to five drops of Hydron II (excess indicator impairs the color change). A bright-rose color develops. Titration is carried out with careful stirring of the solution. The concentration of the sodium ethylenediaminetetracetate solution is varied within the limits 0.02-0.002 N, depending on the mineral content of the water. For the determination of the hardness of water with a very low mineral content by means of 0.002 N sodium ethylenediaminetetracetate, the titration is carried out using a control, in which calcium has been titrated beforehand in an alkali solution, since Hydron II is sensitive to calcium ions contained in it (to 50 ml of distilled water is added 2 ml of 1 N NaOH and this is titrated in the presence of Hydron II).

Hydron II is prepared by mixing one volume of a 0.5% aqueous solution of acid chrome dark green Zh and two volumes of a 0.25% aqueous solution of naphthol yellow.

Both these materials are produced by Russian industry and are used in dye work. The indicator solution does not deteriorate on storage.

SUMMARY

A new indicator containing an internal light filter is proposed for the complexonometric determination of calcium in the presence of magnesium; it is called "Hydron II." The indicator permits determination of calcium in the presence of 100 times its amount of magnesium.

It has been shown that it is possible to determine the calcium hardness of water of low mineral content (5 μg-equiv/liter) using Hydron II as indicator.

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SPECTROGRAPHIC DETERMINATION OF ALUMINUM IN URANIUM

E.A. Vernyi and V.N. Egorov

The difficulties which are encountered during the spectrographic determination of aluminum in uranium are determined, in the main, by the rather low volatility of aluminum oxide, and the very intense and multilinear spectrum of uranium. In view of the latter circumstance, all those methods which are based on the complete burning of the sample in the spectrum excitation source cannot ensure a sufficiently sensitive determination of aluminum. Unsatisfactory results are obtained even when aluminum is determined in uranium by the evaporation method [1-3]. Because of the small difference in the vapor pressure of aluminum oxide and uranoso-uranic oxide, the aluminum does not evaporate completely and this depresses the experimental accuracy considerably. The conditions for evaporating the aluminum improve somewhat on adding carbon powder. However, even in this case, the experimental accuracy is not high. When the sensitivity of the determination of aluminum is $1 \cdot 10^{-3}$%, the reproducibility amounts to 20-30%. Moreover, the given method of determining aluminum, like all other methods based on separating impurities from the main element with their subsequent excitation, is fairly difficult.

Worthy of particular attention for the determination of aluminum in uranoso-uranic oxide is the method of fractional distillation with a carrier, which was used for the first time for uranium by Scribner and Mullin [4]. This method makes it possible to create in the excitation source of the spectrum conditions which will ensure, in the main, that only the impurities are evaporated and excited, so that the spectrum of the base element is thereby weakened appreciably while the spectrum of the impurities is strengthened. In order to excite the spectrum, Scribner and Mullin use a dc arc fed with a current of 10 amp. They used gallium oxide added in amounts of 2% to the test sample as a carrier. The electrode consisted of a graphite basin of a special shape and a carbon support which ensured only a small amount of heat leakage from the sample. The amount of sample taken was 100 mg. The determination was carried out on the basis of the lines Al 3082.16 and 3092.71. The sensitivity of the method amounts to 0.5 γ or $5 \cdot 10^{-4}$% Al.

We have developed a comparatively simple method for determining aluminum in uranium (1 10^{-3} to $3 \cdot 10^{-2}$% Al) using fractional distillation and a carrier.

The success of the method depends to a significant extent on the electrode design. The electrode that proved to be most suitable is the one shown in Fig. 1. Such electrodes ensure rapid and uniform heating of a sample with a very small mechanical increase in the amount of the material in the discharge zone. In choosing a carrier it was desirable to use the same material both as carrier and internal standard. Of the materials tested (AgCl, $SrCO_3$, and $BaCO_3$), barium carbonate proved to be the most suitable. Experiments were carried out to establish the effect of barium carbonate and carbon powder on the intensity of the aluminum lines. The significant effect manifested by carbon powder on the evaporation of aluminum from uranoso-uranic oxide, obviously is the result of a partial reduction of aluminum oxide, with subsequent rapid passing of the aluminum atoms into the discharge zone, as a result of which the aluminum lines increase significantly in strength and the uranium spectrum is weakened. Carbon powder is effective at concentrations of 3% and over. Barium carbonate leads to the same results; however, its mode of action is different. Barium, obviously, while not essentially affecting the evaporation of aluminum from the sample, creates favorable conditions for the excitation of aluminum. This assumption, which is used to explain the role of carrier at present [5, 6] was verified experimentally by us. The experiments which were carried out to check the effect of barium on the line intensity of aluminum, were similar to those which were carried out previously [5]. The electrode used for this purpose is shown in Fig. 2. In one case, a mixture of uranoso-uranic oxide and barium carbonate was placed in the circular crater of the electrode; in another case, the same amounts of uranoso-uranic oxide and barium carbonate were placed separately in the crater. Within the limits of experimental error, the blackening of the aluminum lines proved to be the same in both cases. In addition, the "burning out" of aluminum and barium was studied by photographing the spectra on a moving film. As one might have expected, the aluminum "burnt out" somewhat slower than barium, while the picture was identical in both cases. It should be noted that aluminum is only efficiently excited in the presence of a sufficient amount of barium atoms in the discharge plasma. The aluminum lines weaken on the spectrogram at the same time as the barium lines, and then disappear. Addition of a new lot of barium to the same electrode containing the test sample leads to an increase in the intensity of the aluminum lines. An identical experiment carried out with uranoso-uranic oxide mixed with barium carbonate and 5% of carbon powder, showed that in the presence of carbon powder both aluminum and barium evaporate almost completely from the sample in 20-30 seconds. In this case, addition of a new lot of barium did not lead to the appearance of the aluminum lines.

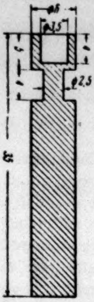

Fig. 1.

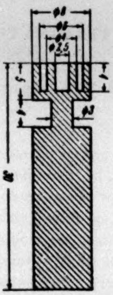

Fig. 2.

From what has been said, it is clear that barium essentially affects the evaporation of aluminum from uranoso-uranic oxide, and significantly improves the excitation conditions of the aluminum atoms.

TABLE 1

Comparison of the Results of Spectrographic and Chemical Methods of Determining Aluminum

Sample	Method		Sample	Method	
	chemical	spectro-graphic		chemical	spectro-graphic
1	$5 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	4	$3.8 \cdot 10^{-2}$	$3.3 \cdot 10^{-2}$
2	$1.1 \cdot 10^{-2}$	$1.3 \cdot 10^{-2}$	5	$2.3 \cdot 10^{-2}$	$2.2 \cdot 10^{-2}$
3	$4 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$	6•	$9 \cdot 10^{-3}$	$1 \cdot 10^{-2}$

•The sample contained 1.3% Mo.

On the basis of the results of these experiments, we chose the following conditions for determining aluminum. Barium carbonate and carbon powder were added to the samples of uranoso-uranic oxide in amounts of 10 and 5%, respectively (100 mg $BaCO_3$ and 50 mg of carbon powder to 1 g of U_3O_8). 25 mg aliquots of test material and standards were placed in the specially designed electrode (Fig. 1). The spectra were excited in an ac arc at a current strength of 18 amp. The upper electrode was a carbon rod sharpened to a truncated cone with an area of 2 mm. Exposure time was 30 seconds. The spectra were photographed on a ISP-51 spectrograph with a UF-85 camera. The slit was illuminated with a one-lens condenser. The slit width was 10-15 μ. The analytical lines Al 3944.03 and Ba 3995.66 are not overlapped by uranium lines.

Calibration curves constructed within the coordinates (ΔS, log C) were linear within the concentrations

$1 \cdot 10^{-3}$ to $3 \cdot 10^{-2}$%. The sensitivity of the determination of aluminum under the conditions chosen is 0.25 γ or $1 \cdot 10^{-3}$% Al, and, when necessary, can be increased. Evaluation of the reproducibility of the method was carried out on samples with aluminum contents of $5 \cdot 10^{-3}$, $1.3 \cdot 10^{-2}$, and $2.2 \cdot 10^{-2}$%. The relative mean-square error of a determination on taking three parallel spectrograms for a sample was 9-11% for this concentration range.

Results of the determination of aluminum by the spectrographic method and by a chemical method are given in Table 1.

TABLE 2

Effect of Third Elements on the Results of Aluminum Determination*

Element	Not introduced	Impurities introduced, %							
		0,1	0,3	1,0	1,3	3	5	7	10
Na (form of Na_2CO_3)	$9 \cdot 10^{-3}$	$8{,}3\ 10^{-3}$	$8{,}5 \cdot 10^{-3}$	$9{,}1 \cdot 10^{-3}$	—	$9{,}5 \cdot 10^{-3}$	—	—	—
CaF_2	$9 \cdot 10^{-3}$	$9{,}7 \cdot 10^{-3}$	$8{,}6 \cdot 10^{-3}$	$9{,}2 \cdot 10^{-3}$	—	$9{,}8 \cdot 10^{-3}$	—	—	—
Fe (form of Fe_2O_3)	$9 \cdot 10^{-3}$	$8{,}7 \cdot 10^{-3}$	$9 \cdot 10^{-3}$	$6{,}5 \cdot 10^{-3}$	—	—	—	—	—
Mo (form of MoO_3)	$9 \cdot 10^{-3}$	—	—	—	$9{,}1\ 10^{-3}$	$8{,}8 \cdot 10^{-3}$	$8{,}3 \cdot 10^{-3}$	$8{,}2 \cdot 10^{-3}$	$6{,}4 \cdot 10^{-3}$

*Mean of 4-5 plates.

The method described, in contrast to the evaporation method, can be used for samples containing large amounts of impurities. The presence of large amounts of barium (7%), which, in the main, determines the excitation conditions of the impurities in the discharge, significantly weakens the effect of third elements. It is clear from Table 2 that no appreciable effect on the results of aluminum determination is shown by CaF_2 (for amounts up to 3%), Fe (up to 0.3%), Na (up to 3%), and Mo (up to 5-7%).

SUMMARY

A spectrographic method which has been developed for the determination of small amounts of aluminum in uranium is based on the phenomenon of fractional distillation with a carrier. Some experiments have been carried out with the aim of studying the effect of barium and carbon powder on the intensity of aluminum lines. The effect of third elements on the results of aluminum determination has been studied.

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**See English translation.

SPECTROGRAPHIC DETERMINATION OF SCANDIUM IN ORES

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Information on the distribution of scandium in nature is mainly based on the results of semiquantitative spectrographic analysis [1]. Known methods for the quantitative spectrographic determination of scandium relate either to the analysis of minerals containing scandium, or to the analysis of monotypic ores, and require in each separate instance the use of appropriate standards similar in composition to the test samples [2-6]. A determination of scandium in which this element was removed beforehand with calcium or thorium, and in which the effect of the composition of the test sample on the analytical results was eliminated, has been described by Solodovik, Rusanov, and Kondrashina [5]. It should be pointed out, however, that preliminary chemical treatment of ores and minerals in order to level the composition of the test samples, and in order to increase the scandium concentration, lengthen the determination considerably, and, in some cases, leaves one in doubt as to whether all the scandium has been separated. Accordingly, methods for the direct determination of scandium in ores are of undoubted interest.

The present article contains a description of a method for the direct determination of thousandths of a percent of scandium in silicate ores, the results obtained being dependent on the composition of the test silicates to a comparatively small extent.

The test ore, diluted with buffer powder consisting of carbon and strontium carbonate, is evaporated in an horizontal ac arc [7] which has been used previously for the quantitative determination of beryllium in ores [10]. Such a position of the electrode ensures uniform passage of the elements into the arc flame, the latter occupying a stable position with respect to the electrodes. The evaporation products are continuously removed by the ascending stream of air from the discharge zone, and do not condense on the upper electrode, as happens when the electrodes are fixed vertically. A characteristic feature of a horizontal arc is the constancy of the distribution of the excitation conditions in the arc cloud during the uniform evaporation of the elements with low ionization potentials which compose the buffer powder.

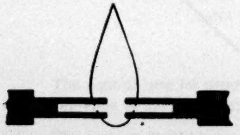

Fig. 1. Graphite electrodes and the image of the arc flame.

During evaporation of silicate ores and products obtained during their technological processing, ash, coal, etc., scandium passes into the arc flame almost at the same time as strontium and those elements located toward the end of the volatility series of the oxides in a carbon arc (rare earths, thorium, niobium, tantalum, zirconium, etc.). The arc is ignited by bringing together the electrode tips and does not require the use of high-frequency currents. After the mixtures of buffer powder and test ore have evaporated, the burning of the arc ceases of itself.

Scandium is determined on the basis of its most sensitive line 4246.83 A, which appears when only ten thousandths of a percent of scandium is present in the test ores. Lanthanum, which is most frequently used for the determination of scandium [3], is used as the standard; lanthanum is added in small amounts in the form of its oxide to the buffer mixture.

The scandium content of the ores is found from the curve relating the logarithm of the relative intensity of the scandium and lanthanum lines to the logarithm of the percentage content of scandium in standards.

The relative intensity of the scandium and lanthanum lines is evaluated by photometric interpolation [8]. This method, which depends to only a small extent on the properties of the photographic plate emulsion, made it possible to obtain a linear calibration curve in the regions of low blackening. The standards used arc powders made by mixing pure scandium oxide with a powder consisting of two parts of quartz and one part of feldspar. Scandium is determined quantitatively in a concentration range from thousandths to hundredths of a percent, with a mean probable error of ±10% when the spectrum of a sample is photographed once.

TABLE 1

Analytical Lines

Analytical lines	Excitation potential of the lines, ev	Concentration range over which scandium is determined, %	Composition of buffer mixture	Dilution of ore by buffer mixture	Interfering elements and control line, A	Error of a single determination, %
Sc II 4246,83, La II 4263,58	3,23 4,86	0,001—0,1	Carbon powder and $SrCO_3$ 1:1	1:3	Ce 1% Ce 4246,4 Ce 4248,6	±10%
Sc II 4246,83, La II 4269,49	3,23 4,69	0,001—0,1	Ditto	1:3	Ce 4248,6	±10%

The analytical lines are given in Table 1.

0.05 g of test ore is mixed with 0.15 g of buffer mixture consisting of equal parts by weight of carbon and strontium carbonate; 0.5% of lanthanum oxide is added to the buffer mixture.

The mixture of powders is carefully ground in an agate mortar in the presence of alcohol. The mixture of powders is evaporated completely from the opening in two carbon electrodes (Fig. 1), the diameter of this opening being 2 mm and its depth 8 mm.

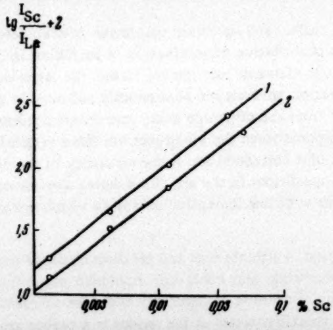

Fig. 2. The relation between the relative intensity of the scandium and lanthanum lines and the scandium concentration of the ore: 1) Sc II – 4246.83 and La II – 4263.58; 2) Sc II – 4246.83 and La II – 4269.49.

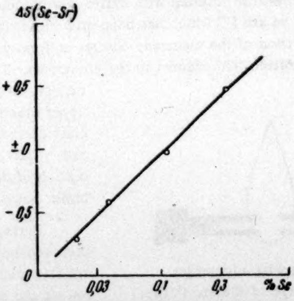

Fig. 3. The relation between the difference in blackening of the lines Sc 2552.36 and Sr 2423.6, and the scandium content of the ore.

The electrodes are fitted up in a horizontal position and an ac arc struck between them (15-amp, 220 volt). The arc gap, which is 4 mm, is kept constant during arc burning. The light from the central part of the arc flame is directed by means of a three-lens illuminating system onto the slit of an autocollimating KS-55 spectrograph fitted with glass optics. The opening in the intermediate diaphragm of the illuminating system is 2 mm.

The spectra are photographed through a ten-stage attenuator fitted in front of the spectrograph slit, on diapositive plates with a sensitivity of 0.8 GOST units. The spectrograms are examined under a spectroprojector, and the equation for the degree of blackening [9] of scandium and lanthanum lines found for each test sample.

Using calculating tables, the blackening is converted to the logarithm of the relative intensity of the analytical pairs of lines:

Sc II 4246.83 and La II 4263.58;

Sc II 4246.83 and La II 4269.49.

In Fig. 2 is shown the calibration curve relating the logarithm of the relative intensity of the pairs of lines to the scandium content of standards.

The experimental results for the scandium content of ores as found by the method described depend only to a small extent on the composition of the ores, and permit analysis of various silicate ores using one series of standards prepared from quartz and feldspar. To illustrate this, there are given in Table 2 analytical results obtained for mineral powders with widely varying contents of silicon, calcium, magnesium, iron, aluminum, and the alkaline metals (feldspar), which usually enter into the composition of silicates.

Changes in the composition of the test material do not affect the results for scandium (Table 2). It should be pointed out that cerium, when present in the ore in amounts upward of 1%, interferes with scandium determination, since the weak line of Ce 4246.4 which is present in the cerium spectrum overlaps the analytical line of scandium.

TABLE 2

Composition of test sample	Scandium		Relative error of a single determination
	taken, %	found, %	
Quartz	0,0185	0,0180	−2,7
Quartz 50% and feldspar 50%	0,0185	0,0180	−2,7
"	0,041	0,042	+2,4
Quartz 50% and Al_2O_3 50%	0,041	0,040	−2,4
Quartz 50% and $CaCO_3$ 50%	0,0060	0,0060	±0
"	0,041	0,045	+9,8
Quartz 50% and MgO 50%	0,0185	0,0190	+2,7
D "	0,041	0,044	+7,3
Quartz 50% and Fe_2O_3 50%	0,0185	0,0190	+2,7
"	0,041	0,036	−12,2

The control line for cerium, the appearance of which indicates the possibility of errors arising as a result of the presence of the overlapping line in the spectrum, is the line Ce 4246.4.

The test ore should not contain more than 0.1% of lanthanum either, since the latter is used as the internal standard and is added in a constant amount to the ore.

When cerium and lanthanum are present, scandium can be determined on the basis of its lines in the ultraviolet; this line is obtained by means of the ISP-22 quartz spectrograph or by the autocollimating KS-55 spectrograph with quartz optics; determinations are based on measurements of the difference in blackening of the lines Sc 2552.36 and Sr 2423.6. The concentration range for which scandium can be determined by the pair of lines indicated is 0.02-0.4%. Iron (in amounts greater than 20%) and thorium (greater than 1%) interfere when scandium is determined by this technique. The appearance of the control line Fe 2553.2 in the spectrum of the ore indicates the danger of overlapping of the Sc 2552.36 by the interfering iron line, while the appearance of the control line Th 2404.17 indicates the danger of the line Sr 2423.6 being overlapped by one of the lines in the thorium spectrum.

The calibration curve relating the difference in blackening of the lines Sc 2552.36 and Sr 2423.6 to the percentage scandium content of the ore is shown in Fig. 3.

SUMMARY

By using as spectrum excitation source a horizontal ac carbon arc stabilized with strontium carbonate, it is possible to determine scandium directly in the concentration range 0.001 to 0.1% in silicate ores of varying composition; the probable error for a single determination is ±10%.

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QUANTITATIVE DETERMINATION OF SCANDIUM BY MEANS OF MANDELIC ACID

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The analytical chemistry of scandium has not hitherto been developed sufficiently [1]. Inorganic precipitants such as hydrogen fluoride, silicofluoric acid, pyrophosphoric acid [2], and hypophosphoric acid [3], etc., have been recommended for the quantitative determination of scandium and for its separation from other elements. Organic precipitants have been studied to a considerably lesser extent; mention could be made of oxalic acid, 8-hydroxyquinoline [4] and its halogen derivatives [5], and sodium alizarinsulfonate [6]. Phytic acid [7] has proved to be the most selective precipitant. Scandium can also be precipitated by phenylarsonic acid. A number of color reactions are also known for scandium, the most interesting of these is the color reaction with azo compounds containing the arsono group [8]. Recently, extraction with organic solvents [9] has been successfully used for separating scandium; ion-exchange chromatography has also been successfully used [10].

Examination of the chemicoanalytical reactions of the scandium ion reveals that it has many properties in common with thorium ions, and, particularly, with zirconium and hafnium ions; the radii of the ions of the last two elements are very similar to the radius of the scandium ion. In addition, scandium ions, just like those of zirconium, tend to polymerize [11]. This fact opens up the possibility of carrying out a search for new reactions and reagents for scandium, using the analogy indicated, and to use differences in the values of the pH of the solution during reactions with organic reagents. Thus, scandium, like thorium and zirconium, can be precipitated by organic derivatives of selenious or tellurious acids [12].

Our experiments have shown that scandium is precipitated in a weakly acid medium by mandelic acid, which, as is known, is a fairly selective reagent for zirconium [13-18]. In the work described in the present article, a study was made of the conditions for precipitating scandium with mandelic acid, and of the composition of the precipitate formed, while a method is described for separating scandium from the rare earths and from thorium.

EXPERIMENTAL

Standard scandium solution. 0.5 g of spectrographically pure scandium oxide was dissolved in 20 ml of concentrated hydrochloric acid with continuous careful stirring until the turbidity disappeared; the solution was carefully evaporated almost to dryness, and the residue dissolved in 500 ml of water. The solution was standardized by precipitating the scandium as hydroxide and weighing it as Sc_2O_3.

Scandium was precipitated with mandelic acid as follows.

To 35 ml of the solution of scandium salt was added 15 ml of an 8% solution of mandelic acid. After heating on a water bath for 30 minutes, and then cooling to room temperature, the white, flocculent precipitate which separated out was filtered, washed with 0.5% mandelic acid solution, dried, and finally calcined at 800° to constant weight.

In order to establish the optimum conditions for precipitating scandium, the effect of the concentration of reagent, and of the pH of the solution was studied. For this purpose, various amounts of an 8% solution of mandelic acid were added to a solution containing scandium (0.00495 g Sc_2O_3), the precipitates formed were then treated as described above. The experimental results obtained are shown in Fig. 1.

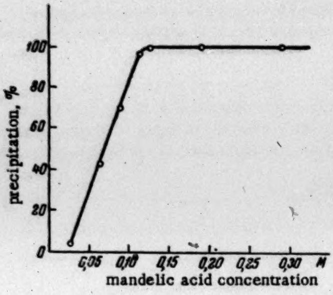


Fig. 1. Effect of mandelic acid concentration on completeness of scandium precipitation.

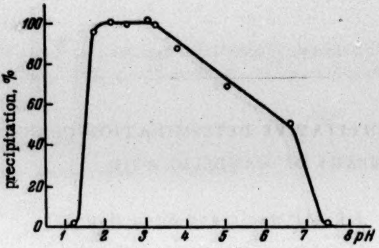
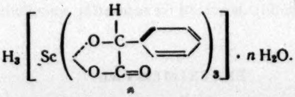


Fig. 2. Effect of pH on completeness of scandium precipitation.

In order to establish the relation between completeness of separation of scandium and the pH of the solution, precipitation with mandelic acid was carried out at various pH values, the pH's being adjusted by means of hydrochloric acid and ammonia. The pH of the filtrates was measured with a glass electrode. The results obtained are given in Fig. 2.

In order to achieve complete precipitation of scandium, it was found necessary to add excess of the reagent, and to maintain the pH of the solution in the range 1.8-3.2. It should be pointed out that zirconium, in contrast to scandium, is precipitated in a solution containing 5-7 N HCl. Results for the quantitative determination of scandium in a solution of its salt are given in Table 1.

Composition and properties of the compound. In order to study the composition of the compound formed between scandium and mandelic acid, the precipitate obtained was filtered through a glass crucible, and washed with a 0.5% mandelic acid solution; traces of mandelic acid were then removed by giving the precipitate a further washing with ether in which it is insoluble; the precipitate was finally dried at 110° and weighed. Part of the precipitate (about 20-50 mg) was calcined to constant weight at 800°, and the oxide Sc_2O_3 obtained, weighed. The results (Table 2) show that the composition of the precipitate isolated from a weakly acid medium (pH 2.5), corresponds to the formula $H_3[Sc(C_8H_6O_3)_3] \cdot nH_2O$. This compound, like zirconium mandelate [13, 19, 20], probably has the following structure:



The precipitates always contain coprecipitated mandelic acid as impurity; accordingly it should be removed by washing with ether before the precipitate obtained is weighed; however, more reliable results are obtained by weighing the scandium oxide obtained by calcining the precipitate.

The thermogram obtained on a continuous thermogravimetric balance (Fig. 3) shows that the compound is stable up to 280°; decomposition is observed at higher temperatures. In the range 340-390° an intermediate compound is formed which changes into scandium oxide at 500°.

The scandium precipitate, like the analogous compounds of zirconium [21] and hafnium [22] is readily soluble in ammonia. We studied the composition of this compound by Hahn's method [22], which was used for studying the similar complex compound of hafnium.

A known amount of the precipitate, obtained as described above, was dissolved in excess of a standard solution of ammonia 0.092 N, after which excess ammonia was titrated with 0.1 N hydrochloric acid using a glass electrode. The experimental results obtained are given in Table 3 and Fig. 4; they give a basis for assuming that dissolution of the precipitate in ammonia follows the following equation:

TABLE 1

Precipitation of Scandium with Mandelic Acid

Sc_2O_3, mg		Error		Sc_2O_3, mg		Error	
taken	found	mg	%	taken	found	mg	%
9,90	9,92	+0,02	20,2	4,95	4,90	−0,05	−1,0
9,90	9,90	±0,00	±0,0	4,95	4,98	+0,03	+0,6
4,95	4,95	±0,00	±0,0	0,99	1,02	+0,03	+2,0
4,95	4,94	−0,01	−0,2	0,99	0,98	−0,01	−1,0

TABLE 2

Analysis of the Compound Formed Between Scandium and Mandelic Acid

Weight of precipitate (mg)	Found, mg		Molar ratio, Sc
	Sc	$C_8H_7O_3$	$C_8H_7O_3$
24,5	2,2	22,3	1:3,0
34,1	3,0	31,1	1:3,1
55,7	4,9	50,8	1:3,1
55,1	4,9	50,2	1:3,0

TABLE 3

Determination of the Composition of the Precipitate after Dissolving it in Ammonia

Weight of precipitate, mg	Total volume of NH_4OH, ml	Volume of HCl solution, ml	Excess NH_4OH, ml	NH_4OH used for dissolving precipitate, ml	Ratio $\frac{NH_4OH}{H_3[Sc(C_8H_6O_3)_3]}$
71,6	25,0	18,4	20,2	4,8	3,1 : 1
105,5	25,0	16,6	18,2	6,8	3,0 : 1
150,4	25,0	13,6	14,9	10,1	3,1 : 1
175,0	25,0	12,5	13,7	11,3	3,0 : 1
226,2	25,0	9,5	10,4	14,6	2,9 : 1

TABLE 4

Determination of Scandium in the Presence of the Rare Earths

Ratio Sc: total rare earths	Sc_2O_3, mg		Error		No. of precipitations
	taken	found	mg	%	
1 : 1	2,97	3,12	+0,15	+5,0	1
	2,97	3,13	+0,16	+5,3	
	2,97	2,97	±0,00	±0,0	2
	2,97	3,01	+0,04	+1,3	
	2,97	2,95	−0,02	−0,7	
1 : 5	2,97	3,15	+0,18	+6,0	2
	2,97	3,10	+0,13	+4,3	
	2,97	3,04	+0,07	+2,3	3
	2,97	2,93	−0,04	−1,3	
1 : 10	2,97	2,96	−0,01	−0,3	3
	2,97	3,03	+0,06	+2,0	

TABLE 5

Determination of Scandium in the Presence of Thorium (Ratio Sc : Th = 1 : 1)

Sc_2O_3, mg		Error		No. of precipitations
taken	found	mg	%	
4,95	4,97	+0,02	+0,4	1
4,95	5,05	+0,10	+2,0	1
2,97	3,02	+0,05	+1,8	1
2,97	3,00	+0,03	+1,0	2

$$H_3[Sc(C_8H_6O_3)_3] + 3NH_4OH \rightleftarrows (NH_4)_3[Sc(C_8H_6O_3)_3] + 3H_2O.$$

The precipitate is also soluble in organic bases such as pyridine and ethylenediamine. Scandium hydroxide is formed by the action of sodium hydroxide. It is clear from the titration curve (Fig. 4) that the precipitate is soluble in ammonia at pH greater than 6.3.

Separation of scandium from the rare earths and thorium. At pH 2-3 the rare earths and thorium do not give a precipitate with mandelic acid; accordingly, it is possible to separate them from scandium. For this pur-

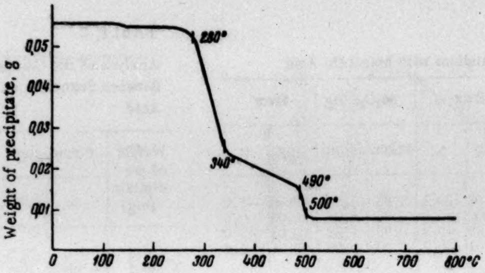


Fig. 3. Thermogravigram of the precipitate $H_3[Sc(C_8H_6O_3)_3] \cdot nH_2O$.

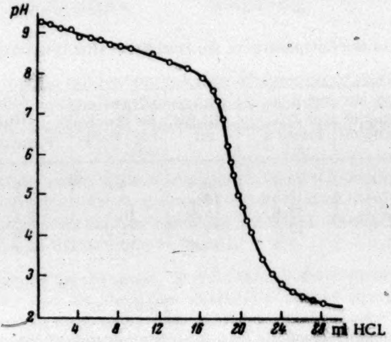


Fig. 4. Potentiometric titration of an ammoniacal solution of scandiomandelic acid with hydrochloric acid.

pose, standard solutions of the nitrates of the rare earths and thorium were taken. Precipitation was carried out as described above. It is necessary to carry out a reprecipitation in order to remove the rare earths quantitatively. For this purpose, the ready solubility of the precipitate in concentrated ammonia was used, the ammonia was added dropwise onto the filter. After washing the filter with distilled water, the solution was neutralized with 4 N HCl until it gave an acid reaction to methyl orange; 15 ml of 8% mandelic acid was added and the solution heated on a water bath for 30 minutes; after cooling, the precipitate was filtered through the same filter.

Results for the determination of scandium in the presence of the rare earths are given in Table 4.

Separation of scandium from thorium was carried out in the same way. It should be noted that large amounts of thorium interfere with scandium determination.

When the pH is increased, coprecipitation of thorium is observed. We tried to complex thorium by means of certain organic acids such as trihydroxyglutaric or lactic acid; however, it was found that scandium is also masked by these acids and does not give a precipitate. Results for the separation of scandium from thorium are given in Table 5.

SUMMARY

A new method has been developed for the quantitative determination of scandium by means of mandelic acid; a method has also been developed for separating scandium from the rare earths and thorium. The composition of the precipitate formed corresponds to the formula $H_3[Sc(C_8H_6O_3)_3] \cdot nH_2O$. The thermogravigram showed that the compound starts to decompose at 280°. Scandium mandelate dissolves in ammonia to form the compound $(NH_4)_3[Sc(C_8H_6O_3)_3]$.

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COLOR AND FLUORESCENT REACTIONS FOR GALLIUM

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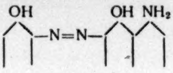
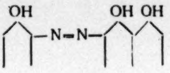
Dyes which had been synthesized by coupling diazo compounds obtained from o-aminophenol and its derivatives, with H-acid [1, 2], were suggested recently as reagents for gallium. The most valuable of these proved to be the reagent which has been called "gallion" [2-3]. It should be pointed out that the reagents suggested have not yet been studied in sufficient detail. Thus, we have not found any information on the effect of pH on the sensitivity, nor any results on the composition of the compounds formed; their use in quantitative analysis, e.g., as complexonometric indicators, etc., has been studied to a comparatively small extent.

Bearing in mind the comparatively small number of known reagents for gallium, we thought that a more detailed study of the reagents indicated might be of undoubted interest. At the same time, we investigated some other dyes differing in composition from gallion.

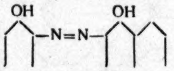
The dyes studied contained the following atomic groups:



(I)



(II)



(III)

It is not difficult to see that there are two hydroxy groups in the o,o' position to the azo group in all the dyes studied. This determines their capacity to react with gallium salts. However, the presence (or absence) of a hydroxy or amino group in the peri position with respect to the ortho hydroxy group leads, as we shall see below, to some characteristic properties in the reaction products formed.

The experiments were carried out on a semimicro scale as follows. To 0.1 ml of gallium nitrate solution (0.1 mg Ga^{3+}) was added 0.1 ml of a buffer solution with a definite pH,* 1-2 drops of a 0.1% aqueous solution of the dye, and any color or fluorescence** which developed on heating to 60-70° observed. A control test was carried out at the same time. Of 68 dyes tested, 22 gave positive reactions for gallium. It was found possible to divide all the reagents into two groups.

The first group includes those reagents which, on interacting with a solution of a gallium salt, form brightly colored compounds. Reagents containing group (I) (Table 1, reagents 1-5) belong to this group.

The second group includes those reagents which give with gallium not only colored, but fluorescent reaction products. These reagents contain atomic groups (II) and (III) (Table 1, reagents 6-9). Table 1 contains only

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*The acetate or ammoniacal buffer solutions were prepared according to published methods [4, 5].

**Fluorescence was observed on illuminating with a mercury quartz lamp provided with a UFS-3 black filter.

TABLE 1

Color and Fluorescent Reactions for Gallium

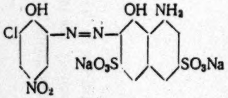
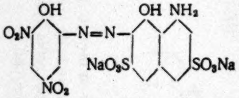
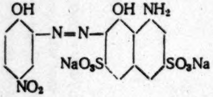
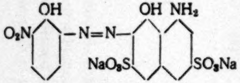
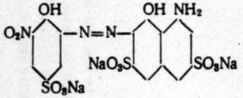
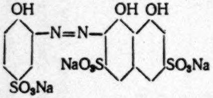
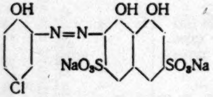
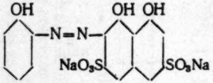
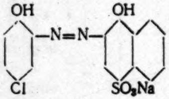
Dye No.	Name	Formula	pH	Color		Fluorescence		Limiting concentration
				control	gallium	control	gallium	
1	Gallion		2—3 4—6	Rose Violet	Pale blue Blue	— —	— —	1 : 1 000 000 1 : 400 000
2	Acid chrome dark-green		3—5	Rose-violet	Blue	—	—	1 : 800 000
3	Palatin chrome green		3—6	Rose	Pale blue	—	—	1 : 800 000
4*	—		2—3 4—6	Rose Violet	Pale blue Blue	—	—	1 : 800 000
5*	—		2—3 4—6	Rose Violet	Pale blue Blue	—	—	1 : 1 000 000

TABLE 1 (continued)

6	Acid chrome blue K		4—8	Red	Violet-red	Violet	Red	1 : 1 000 000
7	Acid chrome dark-green		3—5	Red	Violet	Violet	Red	1 : 700 000
8	Direct blue B		3—5	Red	Violet	Violet	Red	1 : 600 000
9	Acid chrome dark blue 3K		1—5	Red	Violet-red	Red	Bright-rose	1 : 800 000

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*Reagents 4 and 5 do not possess arbitrary names.

TABLE 2

Color Reactions of Some Cations

Dye No.	pH	Control	Cations								
			Ga^{3+}	In^{3+}	Y^{3+}	Th^{4+}	Zn^{2+}	Cd^{2+}	Al^{3+}	Sc^{3+}	La^{3+}
			Color observed								
1	2	Rose	Pale blue	—	—	Violet	—	—	Blue	Violet	—
	3	"	"	Violet	—	"	—	—	"	"	—
	4	Violet	Blue	Blue	—	" "	—	—	" "	" "	—
	5	"	"	"	Red	" "	—	—	" "	Violet-blue	—
	6	" "	" "	" "		" "	Red	Red	" "		—
2	3	Rose-violet	Blue	—	—	—	—	—	—	Violet with a blue tint	—
	4	"	"	Violet	—	Violet-blue	—	—	—		
	5	" "	" "	Blue							
3	3	Rose	Pale blue	—	—	—	—	—	—	Violet	—
	4	"	"	Blue	—	Red	—	—	—	—	—
	5	" "	" "	"	—	"	—	—	—	Blue	—
	6	" "	" "	" "		Violet	Red	—	Violet	"	—
4	2	Rose	Pale blue	—	—	—	—	—	—	Violet	—
	3	"	"	—	—	Violet	—	—	—	"	—
	4	Violet	Blue	Blue	—	"	—	—	—	Blue	—
	5	"	"	"	—	Violet with a blue tint	—	—	—	"	—
	6	" "	" "	" "	—		Blue	—	Rose	" "	—
5	2	Rose	Pale blue	—	—	—	—	—	—	Violet with a blue tint	—
	3	"	"	—	—	—	—	—	—		
	4	Violet	Blue	Blue	Violet with a red tint	—	—	Violet with a red tint	—	Blue	Violet with a red tint
	5	"	"	"					Red	"	
	6	" "	" "	" "		—	—			" "	

TABLE 3

Fluorescent Reactions of Some Cations

Reagent No.	pH	Cations						
		control	Ga^{3+}	In^{3+}	Sc^{3+}	Y^{3+}	Al^{3+}	Th^{4+}
6	4	Violet	Rose	—	Red	—	Rose-raspberry	—
	5	"	"	—	—	—	"	—
	6	» »	» »		Red	Red	» »	Red
	7	» »	» »		"	"	» »	"
	8	Red	» »		» »	» »	» »	» »
7	3	Violet	Red	—	—	—	—	—
	4	"	"	—	—	—	—	—
	5	» »	» »	—	—	—	Red	—
8	3	Violet	Red	—	—	—	—	—
	4	"	"	—	—	—	—	—
	5	» »	« »	—	—	—	Red	—
9	1	Red	Rose	—	Red	—	—	—
	2	"	"	—	"	—	—	—
	3	» »	» »	Bright-red	» »	—	—	—
	4	» »	» »		» »	Red	—	—
	5	» »	» »	» »	» »	Bright-red	—	-

TABLE 4

Determination of the Ratio of the Molar Amounts of Gallium and Gallion in Their Reaction Product

Amount of components, μ mole		Ratio Ga^{3+} : gallion	Optical density
Ga^{3+}	gallion		
0.066	0.334	≈1 : 5	0.13
0.08	0.32	1 : 4	0.17
0.10	0.30	1 : 3	0.22
0.133	0.267	~1 : 2	0.18
0.20	0.20	1 : 1	0.10

those reagents which permit detection of 0.15 γ of gallium and less in 0.1 ml of solution (i.e., a limiting dilution of 1 : 600,000 and less). Only the limiting concentrations for the fluorescent reaction are given for reagents 6-9.

It follows from Table 1 that gallium salts react with the dyes indicated mainly at low pH values. Gallion is one of the most sensitive reagents for gallium. However, a similar sensitivity can be attained when the other reagents are used. The advantage of the second group of reagents is their capacity to give fluorescent as well as color reactions.

Lukin and Zavarakina [2] have noted the effect of substituents in the phenol ring on the analytical properties of the reagents obtained. It is not difficult to see that these properties depend to an even greater extent on the nature of the substituents in the naphthalene ring.

We have also studied the interaction of the dyes tested with some other cations (In^{3+}, Y^{3+}, Th^{4+}, Zn^{2+}, Ce^{3+}, Al^{3+}, Sc^{3+}, La^{3+}, Fe^{3+}).

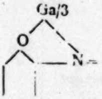
To 0.1 ml (100 γ) of a solution of the salt of the corresponding cation was added 0.1 ml of buffer solution, 1-2 drops of a 0.1% aqueous solution of the dye, and the whole heated to 60-70°; any color or fluorescence which developed was observed (Tables 2 and 3).

It is clear from Tables 2 and 3 that, of the cations listed above, In^{3+}, Sc^{3+}, and Th^{4+}, and also trivalent iron are the ones which mainly interfere with the color reaction for gallium. It is interesting to note that, at low pH values, zinc, cerium, yttrium, and lanthanum ions do not form colored compounds with the given reagents.

We determined the ratio of the molar amounts of gallium and gallion in their reaction product at pH 3 by the isomolar series method. For this purpose, we used 10^{-4} M solutions of gallium and the dye. The solutions were mixed in such proportions that the total amount of the components was equal to 0.4 μmole. The total volume of the test liquid, including the buffer solution, was 5 ml in each case, the layer thickness was 1 cm. A control test was carried out at the same time using the same amount of dye so as to take into account the effect of excess reagent on the color of the reaction product. The optical density was measured on the FEKN-54 photocolorimeter at 610 mμ (Table 4).

Thus, one ion of gallium corresponds to three molecules of dye in the compound formed. Similar tests with other total amounts of gallium salt and gallion led to the same results.

The following formula can, accordingly, be proposed:



We examined the possibility of using the dyes tested as indicators for the complexonometric titration of gallium. Preliminary experiments showed that when a solution of sodium ethylenediaminetetracetate is added to the colored reaction product of gallium with dyes 1, 3, or 5 no color change is observed in the cold. When the solution is heated during titration, a change from blue to rose can be observed.

We standardized the sodium ethylenediaminetetracetate solution by means of a standard solution of a gallium salt.

To 1 ml of a solution of a gallium salt (250 and 350 γ/ml) was added 1 ml of buffer solution (pH 2 in the case of dyes 1 and 5, and pH 3 for dye 3) and one drop of a 0.1% aqueous solution of the dye. The solution was heated to 60-70°, and a 0.01 M solution of sodium ethylenediaminetetracetate added dropwise from a microburet until the color changed.

TABLE 5

Standardization of Sodium Ethylenediaminetetracetate Solution

Dye No.	Amt sodium ethylenediaminetetracetate solution used for titrating gallium, ml		Factor of the sodium ethylenediaminetetracetate as established by means of gallium, mg ml	
	0.35 mg Ga^{3+}	0.25 mg Ga^{3+}		
1	1,05	0,74	0,33	0,34
3	1,07	0,75	0,33	0,33
5	1,08	0,76	0.32	0,30
			Mean	0,33

Thus, under the conditions used, 1 ml of sodium ethylenediaminetetracetate solution corresponds to 0.33 mg gallium (Table 5). These results agree completely satisfactorily with the calculated (theoretical) titer of the sodium ethylenediaminetetracetate as determined against gallium. For determination of 25 γ/ml Ga^{3+} and less we used a solution of sodium ethylenediaminetetracetate which had been diluted ten times. Results for the determination of the gallium content in the test solutions are given in Table 6.

The results obtained show that dyes 1, 3, and 5 can be used as indicators for the complexonometric titration of gallium.

It should be noted that, when Sc^{3+}, Al^{3+}, Zn^{2+}, In^{3+}, and Fe^{3+} are present in solution they interfere with determination of gallium. Thus, complexonometric titration of gallium should be preceded by separation of the latter from the ions listed (e.g., by extraction).

TABLE 6

Complexonometric Determination of Gallium

Ga^{3+} taken, γ/ml	Dye number								
	1	3	5	1	3	5	1	3	5
	amt. sodium ethylenediaminetetracetate solution used for titration, ml			Ga^{3+} found, γ/ml			experimental error, %		
300	0,91	0,90	0,91	301	298	301	0,33	0,66	0,33
200	0,6	0,6	0,61	198,5	198,5	202	0,75	0,75	1
100	0,3	0,31	0,31	99	102,5	102,5	1,0	2,5	2,5
52	0,16	0,15	0,15	53	49,6	53	1,9	4,6	1,9
25	0,78	0,76	0,75	25,7	25,1	24,8	3	0,4	0,8
15	0,45	0,42	0,45	15	14	15	0	6,6	0
10	0,33	0,3	0,27	11	10	9	10	0	10
5	0,15	0,18	0,17	5	6,0	5	0	20	10

SUMMARY

A number of dyes have been suggested as sensitive reagents for gallium.

It has been shown that some of these dyes form colored as well as fluorescent reaction products.

The composition of the compound formed between gallium and gallion has been determined.

It has been shown that some of these dyes can be used as indicators for the complexonometric microdetermination of gallium.

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A NEW REAGENT FOR THE LUMINESCENT DETERMINATION OF GALLIUM

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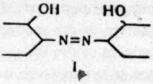
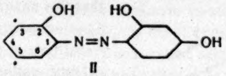
It has been shown in a previous article that the introduction of certain substituents into the molecule of a o,o'-dihydroxyazo compound, which itself has no analytical significance, can convert this compound into a valuable colorimetric reagent. Accordingly, we thought it would be of interest to establish how true this is for luminescent reagents. The opinion has been expressed that a substituent introduced into an organic molecule which can luminesce, can, in most cases, lead to extinction of the luminescence [2]. For example, F, Cl, Br, and I decrease the intensity of the fluorescence of aromatic compounds in the order indicated [3, 4]. The NO_2 group extinguishes fluorescence strongly, and, in almost all cases, leads to its disappearance. In accordance with the views advanced by Lewis and Calvin [2], one might even conclude that the fluorescence in substituted compounds should be less clearly expressed than in unsubstituted compounds.

We could not use a number of compounds obtained earlier [1] for solving the problem confronting us, since, on account of steric hindrance connected with the presence of the sulfo group in the ortho position with respect to the azo group, one could not expect that their complexes with gallium [5] would fluoresce; this assumption was confirmed experimentally. As a consequence, we decided to concentrate on another series of compounds containing group (I), i.e., on those compounds which are obtained by coupling the diazo components obtained from o-aminophenol and its derivatives with resorcinol [formula (II), Table 1]. As substituents, we used the same groups in the same positions with respect to the hydroxy group as before [1]. These positions are marked with asterisks in formula (II) (positions 3 and 5). Synthesis of the azo compounds does not present any difficulties, so that there is no need to describe them. All the compounds obtained were purified by various techniques to a chemically pure state. Twelve azo dyes were prepared in all.*


I


II

All the materials synthesized are compounds which possess a flexible structure; fluorescence develops in them as a result of the clearing of internal radiationless transitions during the formation of inner-complex compounds with cations [6]; we are of the opinion that, in this case, some substituents can favor an increase in the fluorescence of the complexes.

The sensitivity of detection of gallium by means of all these compounds was established directly in aqueous solution, and after extraction of the complex formed with an equal volume of isoamyl alcohol. The optimum pH of the solution [1, 9], which was 3.5, was established by adding a phthalate buffer solution [8]. 0.2 ml of a 0.01% solution of the reagent in acetone was added to 10 ml of test solution. Fluorescence spectra were taken in parallel for solutions containing 0.5 γ gallium. The fluorescence spectra were taken by means of a UM-2 monochromator and a FEU-19 photomultiplier. The fluorescence of the solutions was excited by light from a PRK-2 mercury-quartz lamp fitted with a UFS-3 filter.

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*G.B. Zavarikhina and N.S. Sysoeva took part in the syntheses of the compounds indicated.

TABLE 1

Characteristics of the Fluorescence Reactions Which Develop During the Interaction of Azo Dyes Obtained from Resorcinol [formula (II)] with Gallium Cations

Test No.	Substituent in the positions given in formula II		Sensitivity (γ Ga in 5 ml)	
	3	5	in aqueous solution	in isoamyl alcohol
1	H	H	0.4	0.05
2	H	Cl	0.6	0.1
3	SO_3H	Cl	0.01	0.005
4	NO_2	Cl	–*	–
5	H	NO_2	–	0.01
6	SO_3H	NO_2	–	0.003
7	NO_2	NO_2	–	–
8	Cl	NO_2	–	0.1
9	H	SO_3H	0.05	–
10	SO_3H	SO_3H	0.02	–
11	NO_2	SO_3H	–	–
12	Cl	SO_3H	0.1	–

*The asterisk indicates absence of fluorescence for amounts of gallium up to 1.0 γ.

To supplement published results [5-7], it was established that all the compounds tested do not fluoresce when gallium is absent. When gallium is present, some of them give interaction products which can fluoresce.

It follows from the results obtained (Table 1 and Figs. 1 and 2) that the nature, number, and position* of the substituents introduced have an essential influence on the probability of internal radiationless transitions in the molecules of the inner-complex compounds of the gallium cation with the trihydroxy azo compounds tested, which leads, not only to an increase in this probability, but even to its decrease. Accordingly, the introduction of substituents, as in the case of colorimetric reagents [1], can lead to the creation of valuable luminescent reagents from similar unsubstituted compounds which have no practical importance.

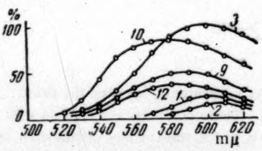

Fig. 1. Fluorescence spectra of aqueous solutions of the compound of gallium with trihydroxyazo compounds. The number on the curves corresponds to the number of the compound in Table 1. The intensity of the fluorescence as compared with the fluorescence of compound 3 at 600 mμ taken as 100%, is plotted along the ordinate.

The nitro group, whatever its position, extinguishes the fluorescence of the inner complex compound in aqueous solution; in isoamyl alcohol, however, the same group, but only in the para position, can lead to a significant increase in the intensity of the fluorescence (compounds 1, 5, 6, and 8).

In the absence of a nitro group, the sulfo group in the para position leads to an increase in the fluorescence in aqueous solution, and to its extinction in isoamyl alcohol (compounds 1, 9, 10, and 12); in the ortho position, the sulfo group behaves differently, depending on the nature of the substituent in the para position (compounds 3, 6, and 10).

The compound of gallium with the mono chloro derivative has a lower intensity of fluorescence, and has a

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*All references to the position of substituents given in the text below are given with respect to the hydroxy group of the diazo component.

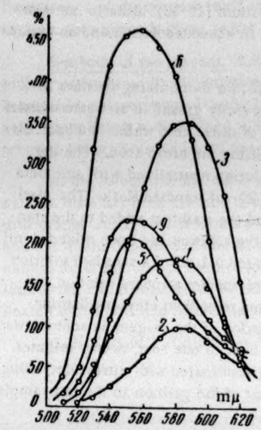
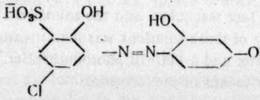


Fig. 2. Fluoresence spectra of the compound of gallium with trihydroxyazo and isoamyl alcohol. The numbers on the curves correspond to the number of the compound in Table 1. The intensity of the fluorescence is given to scale, as is shown in Fig. 1.

spectrum which is shifted toward the long wave side, both in aqueous solution and in isoamyl alcohol (compounds 1 and 2). Additional introduction of a sulfo group into the mono chloro derivative (compound 7), in the ortho position, leads to a reagent whose compound with gallium has a maximum intensity of fluorescence in aqueous solution. Switching these substituents (compound 12) strongly depresses both the sensitivity and the intensity of the fluorescence.

Thus, the combined effect of two substituents cannot be regarded as the sum of the two taken separately. The same conclusion follows from a comparison of the compounds 2, 3, 9, and 10. This conclusion also holds true for the effect of a substituent on the fluorescent properties of the compounds tested, as on the colorimetric properties of compounds studied earlier [1].

Of the greatest interest as a luminescent reagent for gallium is compound 3* (III).



(III)

Although the product formed by the interaction of gallium with compound 6 exhibits a somewhat higher intensity of fluorescence on extraction with isoamyl alcohol, in aqueous solution, however, it does not luminesce. The compound which we chose, namely, 2,2',4'-trihydroxy-5-chloro-1,1'-azobenzene-3-sulfonic acid luminesces in both media on interacting with gallium.

The optimum pH value for development of a luminescent reaction with gallium is 1.7-4.0 both in aqueous solution, and on extraction with isoamyl alcohol. When equal volumes of aqueous solution and isoamyl alcohol are used, the intensity of the fluorescence of the extracted complex is 3.5 times that in the aqueous solution, irrespective of the pH. The reaction sensitivity, both for visual observations of the fluorescence, and when a monochromator with a photomultiplier is used, is 0.01 γ Ga in 5 ml in aqueous solution, while on extracting the complex with isoamyl alcohol (the volume of which is equal to the volume of the aqueous solution), the sensitivity is 0.005 γ Ga in 5 ml. The time taken for maximum fluorescence to develop (for amounts of gallium not exceeding 0.05 γ in 5 ml) is 50-60 minutes, while for amounts of gallium ranging from 0.05-0.5 γ in 5 ml, the time is 25-30 minutes. The intensity of the fluorescence is linearly related to a gallium concentration of up to 0.5 γ in 5 ml of solution, both for the aqueous solution and for the isoamyl alcohol extract.

At pH 2.0-3.0, the fluorescence does not decrease in the presence of Li, Na, K, Cs, NH_4, Ag, Zn, Cd, Hg, Be, Mg, Ca, Sr, Ba, Tl, In, Ge, Pb, As, Sb^{III}, Sb^{IV}, Bi, Cr, Se, Te, Mn, Ru, Co, Th, Nd, Ce, Pr, Ni, Cl^-, NO_3^-, SO_4^{2-}, phthalates, citrates, and acetates, in amounts of 50 γ in 5 ml. Sn, Zr, and Pd in amounts less than 5 γ in 5 ml of solution do not extinguish the luminescence, while Cu, Fe^{III}, Fe^{II}, V, and Mo in amounts less than 0.5 γ in 5 ml of solution do not extinguish the luminescence.

Of the ions listed which, in amounts less than 50 γ in 5 ml of solution, do not decrease the fluorescence, only aluminum gives a fluorescence; however, this fluorescence is considerably less intense than that of gallium. For a ratio of gallium to aluminum of 1 : 1, the latter can be disregarded and measurements are carried out at pH 1.7-3.5. When the amount of aluminum present is ten times that of gallium, interference from aluminum can be removed by establishing a pH of 1.7-2.7, while, when the amount of aluminum is one hundred times that of gallium, it is necessary to work within an even narrower range (pH 1.7-2.2).

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*This reagent is produced commercially under the name "lumogallion IREA."

2,2',4'-Trihydroxy-5-chloro-1,1'-azobenzene-3-sulfonic acid is a more sensitive and selective reagent for gallium than acid chrome blue-black [10-12] or sulfonaphtholresorcinol [13-15]. Of the large number of dihydroxyazo compounds tested as reagents for the luminescent determination of gallium [10-18], hitherto no compound was known which formed a complex with gallium which fluoresces both in aqueous solution and on extraction with an organic solvent.

We used 2,2',4'-trihydroxy-5-chloro-1,1'-azobenzene-3-sulfonic acid [20] for determining gallium in selenium. 100 mg of selenium was weighed out to an accuracy of 1 mg and carefully ground in an agate mortar; it was transferred to a platinum basin and dissolved on gentle warming in 3 ml of nitric acid which had been distilled in a quartz apparatus. The solution was evaporated to dryness without boiling the nitric acid. The dry residue of selenium dioxide was dissolved in 4 ml of distilled water, and the solution neutralized with ammonia to pH 3.0-3.5 using universal indicator paper; this solution was transferred to a 20-ml standard flask. The platinum basin was washed twice with 5 ml of a buffer solution with a pH of 3.0, and the washings added to the standard flask, and the volume made up to the mark with the same solution. After the solution had been mixed, 5-ml aliquots were transferred into four test tubes; into one of these test tubes was added 0.1 ml of a standard solution of gallium containing 1.0 γ/ml Ga, while into another was introduced 0.1 ml of another standard solution containing 0.1 γ/ml Ga; into a third test tube was added 0.1 ml of a 0.01 N solution of sodium ethylenediaminetetracetate, and into a fourth, 0.1 ml of distilled water. 0.2 ml of a 0.01% solution of the reagent in acetone was added to each of the four test tubes, and the solutions allowed to stand for one hour to one hour, twenty minutes. The relative intensity of these solutions was then measured in a 6-ml cuvette (illuminated with ultraviolet) using a UM-2 monochromator and a FEU-19 photomultiplier. The percentage content of the gallium in the test sample (a) was calculated by means of the formula:

$$a = \frac{\Delta C_{\text{Ga}} (I_x - I_T)}{(I_{\text{Ga}} - I_x) n \cdot 2500} \ \%,$$

where ΔC_{Ga} is the amount of gallium introduced in γ; n is the weight of the selenium sample taken in g; I_x is the relative intensity of the fluorescence of the test sample; I_{Ga} is the intensity of the fluorescence of the solution to which gallium has been added; I_T is the reading for the blank solution (with sodium ethylenediaminetetracetate).

For gallium contents less than $5 \cdot 10^{-5}$%, 2.5 ml of isoamyl alcohol is added to each of the test tubes containing the test solution, the sodium ethylenediaminetetracetate, and the added gallium (to 0.01γ), and after shaking, and allowing the layers to separate out, the intensity of the fluorescence of the extracts measured in a 2.5-ml cuvette.

TABLE 2

Determination of Gallium in Selenium

Weight of Se sample, g	Ga added in γ	Ga found, γ in 5 ml	Content, %		Error, %
			calc.	found	
0,106	0,000	0,003	—	$1,1 \cdot 10^{-5}$	—
0,114	0,05	0,018	$5,5 \cdot 10^{-5}$	$6,3 \cdot 10^{-5}$	+15
0,122	0,05	0,017	$5,3 \cdot 10^{-5}$	$5,6 \cdot 10^{-5}$	+ 6
0,104	0,10	0,026	$1,1 \cdot 10^{-4}$	$1,0 \cdot 10^{-4}$	— 9
0,094	0,10	0,024	$1,2 \cdot 10^{-4}$	$1,02 \cdot 10^{-4}$	—15
0,124	0,20	0,048	$1,7 \cdot 10^{-4}$	$1,5 \cdot 10^{-4}$	—12
0,111	0,20	0,050	$1,9 \cdot 10^{-4}$	$1,9 \cdot 10^{-4}$	0

Results for the determination of gallium in selenium are given in Table 2, from which it is clear that the experimental error does not exceed 15%.

The suggested reagent is also suitable for the purification of the solutions of a number of salts from micro amounts of Al, Cu, Fe, etc., present as impurities, by sorbing their inner-complex compounds by means of activated charcoal or with anion exchange resins [19]. For example, an acetate buffer solution with a pH of 6.0 can be purified from aluminum in contents up to $5 \cdot 10^{-8}$%.

It should be pointed out that the reagent suggested exhibits its highest efficiency (complete absence of fluorescence of the reagent itself under the analytical conditions used) after a special acid purification. Accordingly, a description is given below of the synthesis and purification of the reagent.*

Synthesis of the reagent. 2.2 g of resorcinol with a m.p. of 110° is dissolved in 60 ml of a 10% solution of sodium carbonate. To this solution is added a solution of the diazo compound obtained as follows: 4.4 g of pure 2-amino-4-chlorophenol-6-sulfonic acid is added to 30 ml of water and acidified with 2-3 drops of hydrochloric acid, the solution is diazotized with a solution of 1.4 g of sodium nitrite in 10 ml of water, the progress of the reaction being controlled with starch iodide paper and congo paper.

As the solution of the diazo compound is added, the reaction mass becomes red. After coupling is complete and the mass has been allowed to stand for 2-3 hours, it is acidified with hydrochloric acid; at this stage, a reddish-orange amorphous precipitate separates out. The latter is filtered off and transferred into 150 ml of water and the whole then heated almost to the boiling point; to the hot suspension is added 20 ml of concentrated hydrochloric acid; the orange needles formed (visible under the microscope) are filtered in the hot state, and again transferred into a mixture of 50 ml of water and 20 ml of concentrated hydrochloric acid; the suspension is again heated to the boil and filtered in the hot state, after which the material is dried to constant weight at 80-90°.

$C_{12}H_{10}O_6N_2SCl$. Calculated %: Cl 10.29; S 9.30. Found %: Cl 10.41, 10.51; S 9.27, 9.09.

SUMMARY

A study has been made of the effect of substituents on the luminescent properties of the compounds of gallium with trihydroxyazo compounds obtained by coupling resorcinol with the diazo component from o-aminophenol and its derivatives.

Of the substituted derivatives studied, the most promising as a reagent for the luminescent determination of gallium is 2,2',4'-trihydroxy-5-chloro-1,1'-azobenzene-3-sulfonic acid.

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SEPARATION OF INDIUM AND GALLIUM BY MEANS OF DIETHYLDITHIOCARBAMATE

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Comparatively few methods have been suggested for the separation of indium and gallium [1-8]. The methods suggested include methods based on extraction with organic solvents [1, 7, 9-13] and chromatographic methods [14-19]. In practice, indium and gallium are separated almost exclusively by the cupferron method, and by extraction of gallium chloride with ether [2, 9]. Other methods do not give reliable results, are characterized by difficulties in carrying them out, and, in some cases, the methods have not been developed sufficiently. Accordingly, there is need for simple, accurate, and reliable methods of separating elements which are as similar in properties as indium and gallium. We have established that under certain conditions it is possible to separate indium and gallium successfully by means of sodium diethyldithiocarbamate.

Sodium diethyldithiocarbamate forms sparingly soluble precipitates with indium and gallium, and also with elements which give stable sulfides in aqueous solution. Indium is quantitatively precipitated at pH 1.5-9, but is not precipitated from HCl (1 : 1), and from concentrated HCl [20]. During the gravimetric determination of indium in the form of $[(C_2H_5)_2NCS_2]_3In$, it is precipitated with sodium diethyldithiocarbamate at a pH of 4-5, and the precipitate dried at 105° [21, 22]. Patrovskii [23] precipitated indium with sodium diethyldithiocarbamate at pH 7-11 from a solution containing tartrate and cyanide. Thus, it is possible to determine indium in the presence of Al, Ga, Cu, Zn, Cd, and Sn. Indium diethyldithiocarbamate is quantitatively extracted with ethyl acetate at pH 3 [20]. Bode [24] established that indium diethyldithiocarbamate is almost completely extracted with carbon tetrachloride at pH 5-10 from a solution containing tartrate. Potassium cyanide does not affect the extraction. Sodium ethylenediaminetetracetate interferes with the extraction (at pH > 7, indium diethyldithiocarbamate is not extracted at all; at pH 5-7, it is extracted partially). A solution of indium diethyldithiocarbamate in CCl_4 absorbs light in the ultraviolet; the absorption maximum is observed at 305 $m\mu$. It has been suggested that it should be possible to determine indium photometrically by converting the colorless compound $[(C_2H_5)_2NCS_2]_3In$ into the colored compound $Cu[(C_2H_5)_2NCS_2]_2$ [23, 24]. Other disubstituted dithiocarbamates also precipitate indium [25]. This is used, for example, for concentrating traces of indium [26].

Gallium is precipitated by sodium diethyldithiocarbamate at pH 1.5-6 in the form of a white precipitate which is soluble in ethyl acetate [20]. Gallium diethyldithiocarbamate is quantitatively extracted with ethyl acetate at pH 3 [20]. During a study of the interaction of dithiocarbamic acid and its disubstituted salts with the salts of Al, Ga, and In, it was established that aluminum does not give a diethyldithiocarbamate, gallium gives a readily hydrolyzed diethyldithiocarbamate, while indium diethyldithiocarbamate is stable in the presence of water [25].

Bode [24], while studying the behavior of sodium diethyldithiocarbamate toward various elements, established that gallium diethyldithiocarbamate is only extracted with CCl_4 at pH < 5.5, at which value the reagent itself starts to break down. Sodium ethylenediaminetetracetate interferes with the precipitation and extraction. Bode came to the conclusion that sodium diethyldithiocarbamate is not suitable for the quantitative determination of gallium or for its separation from other elements. Some authors have indicated that sodium pyrollidinedithiocarbamate is more suitable for determining gallium and for separating it from other elements [26, 27]. The fact that gallium pyrollidinedithiocarbamate can be extracted at pH 4.8 with chloroform is used for concentrating gallium [26]. A method has been developed for the gravimetric and nephelometric determination of gallium by means of sodium pyrollidinedithiocarbamate [28].

Solutions and reagents. 1. Solutions of gallium and indium nitrates were prepared by dissolving the spectrographically pure metals in the minimum amount of concentrated HNO_3. After dilution with water, the pH of the solution was 1-2. The solutions were standardized by the hydroxyquinoline method [29]. 1 ml of solution contained about 1 mg of Ga and 2.5 mg of In.

2. A 2% aqueous solution of sodium diethyldithiocarbamate "pure" grade.

3. Buffer solutions were prepared by the usual method [30]:

$0,2M\ CH_3COOH + 0,2M\ CH_3COONa$,	pH 3,72—5,57,
$0,2M\ KCl + 0,2M\ HCl$,	pH 1,00—2,20,
$0,2M\ H_3BO_3 + 0,05M\ Na_2B_4O_7$,	pH 7,09—9,11.

Interaction of Gallium and Indium Ions with Sodium Diethyldithiocarbamate, and the Properties of the Compounds Formed

The white precipitate formed on addition of sodium diethyldithiocarbamate to a solution of gallium nitrate was filtered off, washed with water, and then heated in a drying oven. It was found that at temperatures above 150° there was observed a sharp decrease in weight; presumably, the precipitate starts to decompose. The gallium and nitrogen content of the precipitate dried at 110-140° to constant weight was determined. In order to determine gallium, the precipitate was treated with HNO_3 (1 : 1) on heating, the solution was evaporated to dryness, and the residue was dissolved in water, and the gallium precipitated with 8-hydroxyquinoline [29]. Nitrogen was determined by the Kjeldahl method.

13.60, 13.82, 13.38, and 13.80% of Ga – an average of 13.65% – and 7.80, 7.89% of nitrogen – an average of 7.85% – was found. The theoretical values for $Ga[(C_2H_5)_2NCS_2]_3$ are 13.55% Ga and 8.17% N. The gallium content of the precipitate was also determined by calcination (carefully at first) of an aliquot at 800-1000°. Quantitative formation of Ga_2O_3 thereupon occurs. 0.2368, 0.2220, and 0.1944 g of the precipitate dried at 110 to 140° were taken; 0.0428, 0.0412, and 0.0356 g of Ga_2O_3 were obtained.

13.38, 13.80, and 13.60% Ga – a mean value of 13.60% Ga – was found, which is in good agreement with the expected amount.

Thus, on mixing solutions of gallium salt and sodium diethyldithiocarbamate, gallium diethyldithiocarbamate is actually formed. After drying at 110-140°, its composition corresponds to the formula $Ga[(C_2H_5)_2NCS_2]_3$.

Gallium diethyldithiocarbamate is soluble in alkalis and ammonia; it is precipitated again from alkali solutions on careful acidification. Acids (HCl, H_2SO_4, and HNO_3) decompose the precipitate. Concentrated acids decompose the precipitate immediately. Concentrated acetic acid in the cold does not affect gallium diethyldithiocarbamate; on heating, it dissolves. Gallium diethyldithiocarbamate is partially decomposed by water on heating; decomposition is particularly significant on boiling. Gallium diethyldithiocarbamate readily dissolves in organic solvents: chloroform, carbon tetrachloride, ethyl acetate, and amyl acetate.

A study of the precipitation of gallium by sodium diethyldithiocarbamate at various pH's was carried out as follows: to a weakly nitric acid solution of gallium nitrate was added a buffer solution in order to establish a definite pH; a 2% aqueous solution of sodium diethyldithiocarbamate was then added in fivefold excess. An indicator was added to control the pH. Since an aqueous solution of sodium diethyldithiocarbamate has a strongly alkaline reaction because of hydrolysis, on addition of this reagent, the pH increases somewhat. The precipitate was filtered off after 30 minutes, washed with water, and dried at 110-140°. The conversion factor to gallium is 0.1355. The pH of the filtrate was determined with a glass electrode.

At pH > 8.5, gallium diethyldithiocarbamate is not precipitated at all. When an alkaline solution (pH > 9) containing gallium and sodium diethyldithiocarbamate is carefully neutralized with acid, then, at pH about 8.3, a precipitate of gallium diethyldithiocarbamate starts to separate out. When gallium diethyldithiocarbamate is precipitated at pH 8-8.3, and alkali or ammonia then added until the pH is greater than 8.3, the precipitate only dissolves partially. As is evident from Table 1, gallium diethyldithiocarbamate is precipitated quantitatively at pH 2.7-5.0. Despite this, determination of gallium as its diethyldithiocarbamate would not seem to be of much practical significance because of the poor selectivity; indium, iron, zinc, and other elements interfere. Tartaric and sulfosalicylic acids do not affect precipitation of gallium diethyldithiocarbamate (Tables 2 and 3) in the pH

TABLE 1

Effect of pH of the Solution on the Precipitation of Gallium Diethyldithiocarbamate*

pH of filtrate	Ga taken, mg	Weight of precipitate, g	Ga found, mg	Error	
				absolute, mg	%
1,06	4,87	0,0204	2,76	−2,11	−43,3
2,00	4,87	0,0280	3,79	−1,08	−22,1
2,67	4,79	0,0358	4,85	+0,06	+ 1,2
3,28	4,77	0,0346	4,68	−0,09	− 1,9
4,60	4,69	0,0342	4,63	−0,06	− 1,2
5,00	4,77	0,0350	4,73	−0,04	− 0,8
5,79	4,77	0,0318	4,31	−0,46	− 9,6
6,00	4,77	0,0316	4,28	−0,49	−10,2
7,00	4,77	0,0290	3,92	−0,89	−18,9
8,00	4,77	0,0262	3,55	−1,22	−25,5

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*In all cases, at pH > 4, sodium tartrate was added to the solution to prevent precipitation of gallium hydroxide.

TABLE 2

Effect of Sodium Tartrate on Precipitation of Gallium Diethyldithiocarbamate (pH 4)

Taken				Molar ratio tartrate:Ga	Wt. of precipitate, g	Ga found, mg	Error	
Ga		sodium tartrate						
mg	mmole per liter	mg	mmole per liter				abs., mg	%
5,15	1,84	50	6,4	3,4 : 1	0,0383	5,18	+0,03	+0,6
5,15	1,84	100	12,8	7 : 1	0,0376	5,09	−0,06	−1,2
5,15	1,84	250	32,2	17 : 1	0,0381	5,16	+0,01	+0,2
5,15	1,84	500	64,5	35 : 1	0,0378	5,12	−0,03	−0,6
5,15	1,84	1000	129,0	70 : 1	0,0376	5,09	−0,06	−1,2

TABLE 3

Effect of Sodium Sulfosalicylate on the Precipitation of Gallium Diethyldithiocarbamate (pH 4.4)

Taken				Molar ratio, sulfosalicylate:Ga	Wt. of precipitate, g	Ga found, mg	Error	
Ga		sodium sulfosalicylate						
mg	mM/liter	mg	mM/liter				abs., mg	%
3,86	1,38	60	7,2	5 : 1	0,0282	3,82	−0,04	−1
5,15	1,84	300	36	20 : 1	0,0380	5,14	−0,01	−0,2
5,15	1,84	600	72	39 : 1	0,0378	5,12	−0,03	−0,6
3,87	1,38	1000	121	88 : 1	0.0282	3,82	−0,05	−1,3

range in which precipitation of the latter occurs from the usual solutions. Gallium is precipitated incompletely with sodium diethyldithiocarbamate in the presence of small amounts of sodium oxalate, while in the presence of large amounts of the sodium oxalate it is not precipitated at all (Table 4).

Our experiments confirmed published data [1, 20, 22, 23] on the quantitative precipitation of indium by sodium diethyldithiocarbamate within a wide pH range; tartaric acid does not affect its precipitation. Sulfosalicylic acid and sodium oxalate do not interfere with the quantitative precipitation of indium (Tables 5 and 6).

TABLE 4

Effect of Sodium Oxalate on the Precipitation of Gallium Diethyldithiocarbamate (pH 2.7-5.0)

Taken				Molar ratio, $C_2O_4^{2-}$:Ga	Wt. of precipitate, g	Ga found, mg	Error	
Ga		sodium oxalate					abs., mg	%
mg	mmole per liter	mg	mmole per liter					
2,86	1,08	22,2	4,1	3 : 1	0,0144	1,95	-0,91	— 32
5,15	1,84	59,2	11,04	6 : 1	0,0206	2,79	—2,36	—45,7
5,15	1,84	148,0	27,60	15 : 1	—	—	—	—

TABLE 5

Effect of Sodium Sulfosalicylate on the Precipitation of Indium Diethyldithiocarbamate (pH 4.0). Conversion factor to indium 0.2050

Taken				Molar ratio, sulfosalicylate:In	Wt. of precipitate, g	In found, mg	Error	
In		sodium sulfosalicylate					abs., mg	%
mg	mmole per liter	mg	mmole per liter					
5,92	1,2	400	48,0	40 : 1	0,0288	5,90	—0,02	—0,3
5,92	1,2	800	96,0	80 : 1	0,0282	5,78	—0,14	—2,3
5,33	1,2	800	96,0	80 : 1	0,0257	5,27	—0,06	—1,0

TABLE 6

Effect of Sodium Oxalate on the Precipitation of Indium Diethyldithiocarbamate (pH 3-4)

Taken				Molar ratio, $C_2O_4^{2-}$:In	Wt. of precipitate, g	In found, mg	Error	
In		sodium oxalate					abs., mg	%
mg	mmole per liter	mg	mmole per liter					
5,98	1,3	25,9	4,8	3,7 : 1	0,0293	6,00	+0,02	+0,3
5,98	1,3	52,0	9,6	7 : 1	0,0292	5,98	0,00	0,0
5,98	1,3	122,1	22,8	18 : 1	0,0288	5,90	—0,08	—1,2
5,98	1,3	244,2	45,5	35 : 1	0,0291	5,97	—0,01	—0,2

A Study of the Extraction of Gallium and Indium Diethyldithiocarbamates

Chernikhov and Dobkina [20] have noted that gallium diethyldithiocarbamate is extracted at pH 3 by ethyl acetate. 100 γ out of 120 γ originally taken was found in the ester phase. Gallium diethyldithiocarbamate is also extracted by $CHCl_3$, CCl_4, and other organic solvents. Extraction is carried out best of all with ethyl acetate, the layers separate out rapidly and no foam is formed on the phase boundary, as occurs in the case of $CHCl_3$. We carried out the extraction in a 100 ml separating funnel as follows: to a solution of a gallium salt was added in succession a buffer solution, a 2% solution of sodium diethyldithiocarbamate taken in a fivefold excess, and ethyl acetate; the whole was shaken for two minutes; after separation of the layers, the gallium content was determined by means of 8-hydroxyquinoline. In order to determine gallium, the ester extract was evaporated to dryness on a water bath, the dry residue was then treated with HNO_3 (1 : 20) and then evaporated to dryness again. The dry residue was dissolved in water and gallium determined. The extractability of indium diethyldithiocarbamate was studied in the same way.

As is evident from Table 7, gallium diethyldithiocarbamate is almost completely extracted with one portion of ethyl acetate at pH 1.5-5. Starting at a pH of 6, more and more of the gallium remains in the aqueous

TABLE 7

Effect of the pH of the Aqueous Solution on the Extraction of Gallium Diethyldithiocarbamate by Ethyl Acetate (the pH of the aqueous solution was measured with a glass electrode)

Acidity of the aqueous solution	Ga taken, mg	Ga found, mg		Extr. Ga	Acidity of the aqueous solution	Ga taken, mg	Ga found, mg		Extr. Ga
		in the ester layer	in the aqueous layer				in the ester layer	in the aqueous layer	
1*N* HCl	3,87	—	3,83	—	pH4,57	3,87	3,86	—	99,7
pH 1,35	5,78	5,40	0,64	93,42	4,70	5,78	5,79	—	100,17
1,61	5,78	5,76	—	99,65	5,86	5,78	4,90	0,71	84,77
2,15	2,90	2,94	—	101,1	6,70	5,78	4,39	1,11	75,95
2,91	5,78	5,83	—	100,56	7,51	5,78	2,99	2,78	51,73
3,85	3,87	3,88	—	100,20	8,15	5,78	0,61	5,15	10,55
4,15	5,78	5,64	0,19	97,57					

TABLE 8

Effect of $Na_2C_2O_4$ on the Extraction of Gallium Diethyldithiocarbamate with Ethyl Acetate (pH 3.4-4)

Taken				Molar ratio, $C_2O_4^{2-}$:Ga	Ga found, mg		% Ga extracted
Ga		sodium oxalate			in the ester layer	in the aqueous layer	
mg	mmole per liter	mg	mmole per liter				
5,78	2,07	33,23	6,20	3 : 1	5,41	0,21	93,59
5,78	2,07	66,50	12,40	6 : 1	3,08	2,44	53,28
5,78	2,07	166,5	31,06	15 : 1	—	5,80	0

TABLE 9

Effect of $Na_2C_2O_4$ on the Extraction of Indium Diethyldithiocarbamate with Ethyl Acetate (pH of the aqueous layer 4)

Taken				Molar ratio, $C_2O_4^{2-}$:Ga	In found, mg		% In extracted
In		sodium oxalate			in the ester layer	in the aqueous layer	
mg	mmole per liter	mg	mmole per liter				
4,74	1,03	18,5	3,4	3 : 1	4,66	—	98,31
4,74	1,03	37	6,8	7 : 1	4,56	—	96,20
4,74	1,03	92,5	17	17 : 1	4,62	—	97,45
7,74	1,03	185	34	34 : 1	4,69	—	98,95

phase, and already, as early as pH > 8, almost all the gallium remains in the aqueous phase. Comparison of the results given in Tables 1 and 7 shows that the pH range for the quantitative precipitation and extraction of gallium diethyldithiocarbamate almost coincide. Tartaric and sulfosalicylic acids do not affect the extraction. Oxalic acid prevents extraction of gallium diethyldithiocarbamate (Table 8).

Our experiments confirmed published data [20, 23] relating to the quantitative extraction of indium diethyldithiocarbamate with one portion of ethyl acetate at a pH of 3-10. Tartaric, sulfosalicylic, and oxalic acids do not interfere with the extraction of indium diethyldithiocarbamate with ethyl acetate.

Technique for Separating Indium and Gallium

A comparison of the results given in Tables 4 and 6, 8 and 9 shows that indium and gallium can be separated at pH 3-5, if the indium diethyldithiocarbamate is precipitated and is extracted with ethyl acetate in the

TABLE 10

Precipitation of Indium with Sodium Diethyldithiocarbamate in the Presence of Gallium (at pH 3-4) on Addition of Excess Oxalate

Taken, mg		Ratio, In:Ga	In found mg	Error in determining In		Ga found, mg	Error in determining Ga	
In	Ga			abs., mg	relative, %		abs., mg	relative, %
2,39	19,68	1 : 8	2.44	+0,05	+2,1	19,89	+0,21	+1,06
2,39	19,68	1 : 8	2.46	+0,07	+2,9	19,82	+0,14	+0,7
2,99	4,92	1 : 2	2,97	−0,02	−0,7	4.93	+0,04	+0,8
5,98	4,92	1 : 1	5.79	−0,19	−3,1	4,94	+0,02	+0,4
5,98	4,92	1 : 1	5,96	−0,02	−0,3	4,96	+0,04	+0,8
5,98	4,92	1 : 1	6,03	+0,05	+0,8	4,79	−0,13	−2,6
5,98	4,92	1 : 1	6.04	+0,06	+1,0	4,93	+0,01	+0,2
5,98	2,46	2 : 1	6,01	+0,03	+0,5	2,30	−0,16	−3,3
5,98	2,46	2 : 1	5,90	−0,08	−1,3	2,50	+0,04	+0,8

TABLE 11

Separation of Indium and Gallium by Extraction of Indium Diethyldithiocarbamate with Ethyl Acetate in the Presence of Excess Oxalate (pH 3-5)

Taken, mg		Ratio, In:Ga	In found, mg	Error in determining In		Ga found, mg	Error in determining Ga	
In	Ga			abs., mg	relative, %		abs., mg	relative, %
4,74	5,78	1 : 1	4,74	—	—	5,80	+0,02	+0,3
2,84	5,78	1 : 2	2,85	+0,01	+0,4	5,80	+0,02	+0,3
2,94	15,02	1 : 5	3,00	+0,06	+2,0	14,96	−0,06	−0,4
2,94	30,04	1 : 10	2,96	+0,02	+0,7	29,97	−0,07	−0,2

presence of excess sodium oxalate.• To a solution containing 2-6 mg of In and 2.5-30 mg Ga is added sodium oxalate or oxalic acid. For each milligram of In or Ga 20-30 mg of sodium oxalate or oxalic acid is added (15 moles of oxalic acid or sodium oxalate per mole of In or Ga). The solution is neutralized with ammonia, using methyl orange as indicator. A 2% aqueous solution of sodium diethyldithiocarbamate (usually, it is taken in a two- to three-fold excess) is then added with stirring. The solution plus the precipitate of indium diethyldithiocarbamate is allowed to stand for 8-24 hours, and the precipitate then filtered through a No. 3 or No. 4 glass crucible; it is washed with water and dried to constant weight at 105° and weighed. The conversion factor to In is 0.2050. Gallium is determined in the combined filtrates and wash liquors by precipitation with 8-hydroxyquinoline.

Indium and thallium can be separated by an extraction method. 10-30 ml of ethyl acetate is added and the whole shaken for two minutes. The phases are allowed to separate and the ester phase evaporated to dryness on a water bath, the residue is treated with HNO_3 (1 : 20) and again evaporated to dryness; the dry residue is dissolved in a small volume of water and indium precipitated with 8-hydroxyquinoline. As is evident from Tables 10 and 11, the results obtained during the separation of indium and gallium are completely satisfactory. The average error is 1-2%.

Completeness of separation of the precipitates of indium diethyldithiocarbamate and gallium and indium 8-hydroxyquinolates was investigated spectroscopically. Indium diethyldithiocarbamate was calcined to In_2O_3 at 800-1000°, while indium and gallium 8-hydroxyquinolates were calcined with oxalic acid. The spectra were photographed on an ISP-22 spectrograph, the spectra being excited in an ac arc, while the exposure time was 30 seconds. Examination of the spectra showed that the In content of the Ga_2O_3 was of the order of 10^{-3}%, while the

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•According to the results of some authors [31-35], indium and gallium ions form complex ions with oxalate ions.

Ga content of the In_2O_3 was 10^{-2} to 10^{-3}%, i.e., for the amounts of In and Ga taken, the amount of one element present as an impurity in the other is of the order of 0.0001-0.0005 mg. Thus, the fact that accurate results are obtained for indium and gallium is not a result of compensation of errors.

Aluminum does not interfere with the separation of indium from gallium, while iron, both ferrous and ferric, behaves like indium, i.e., sodium oxalate does not interfere with the precipitation and extraction of Fe and In diethyldithiocarbamates. Accordingly, indium will be precipitated and extracted together with iron in the presence of sodium oxalate.

SUMMARY

Gallium diethyldithiocarbamate is precipitated at pH 1-8.5, while at pH 2.7-5.0 the precipitation is quantitative. Gallium diethyldithiocarbamate is extracted quantitatively by ethyl acetate at pH 1.5-5. Tartaric and sulfosalicylic acids do not affect either the precipitation or the extraction. Oxalic acid prevents precipitation and extraction.

Indium diethyldithiocarbamate at pH 3-10 is quantitatively precipitated and quantitatively extracted by ethyl acetate. Tartaric, sulfosalicylic, and oxalic acids do not affect the precipitation and extraction.

A technique has been developed for separating indium and gallium; it is based on precipitation of indium diethyldithiocarbamate, or on its extraction with ethyl acetate at pH 3-5 in the presence of excess oxalate. For ratios of In : Ga up to 1 : 10, the error for In and Ga is ±1-3%.

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DETERMINATION OF RARE EARTHS PRESENT AS IMPURITIES IN SAMARIUM AND EUROPIUM

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The present article contains a description of a method for the quantitative determination of rare-earth elements and yttrium present as impurities in pure samarium and europium oxides. There is very little published data on the analysis of europium and samarium. Tassel [1, 2] has developed a technique for the determination of europium and samarium on a spectrograph with the high dispersion of 2.5 A/mm.

Kryuger and Shvangiradze [3] analyzed samarium for europium using the ISP-22 spectrograph, which has average dispersion.

For production control, a technique is required for the total quantitative analysis of europium and samarium oxides for their content of all the rare earths and yttrium. Such a technique should not only be sufficiently sensitive and accurate, and should not require a large amount of the very pure oxides of the rare earths, but the time taken to carry out an analysis should also be as short as possible. The purpose of the work described here was to develop such a method. In order to cut down on the time taken, the analysis is carried out in two stages: the elements of the cerium group are determined simultaneously in samarium and europium, while the elements of the yttrium group are also determined simultaneously. The method described below is applicable in the concentration range from the limit of detection to 5%.

The method chosen was emission spectrographic analysis from solutions. A drop of test solution was placed on the end of a graphite electrode which had been treated beforehand with a 3% solution of polystyrene in benzene, and the whole dried at 100° [4].

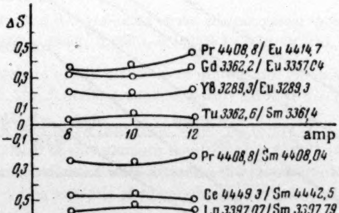

Fig. 1.

Apparatus and excitation conditions. The work was carried out on a DFS-3 diffraction spectrograph with a dispersion of 2 A/mm throughout the whole range. The spectra were excited in an ac arc with a current of 10 amp. The very close similarity in the behavior of many of the rare earths during excitation in the arc ensures a high degree of internal standardization of random variations during excitation in an ac arc.

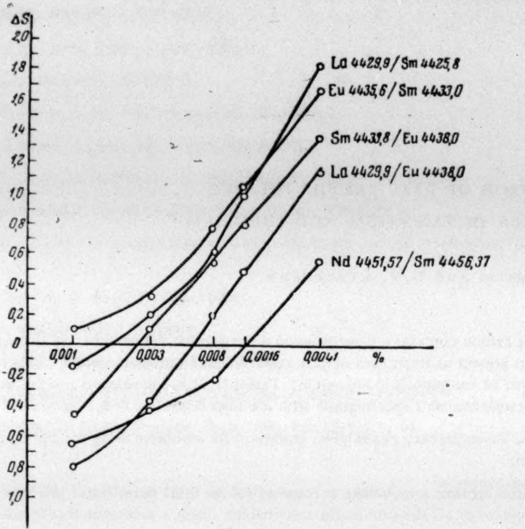
ΔS
2,0
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0
0,2
0,4
0,6
0,8
1,0
0,001
0,003
0,008
0,0016
0,0041
%
La 4429,9 / Sm 4425,8
Eu 4435,6 / Sm 4433,0
Sm 4431,8 / Eu 4438,0
La 4429,9 / Eu 4438,0
Nd 4451,57 / Sm 4456,37

Fig. 2.

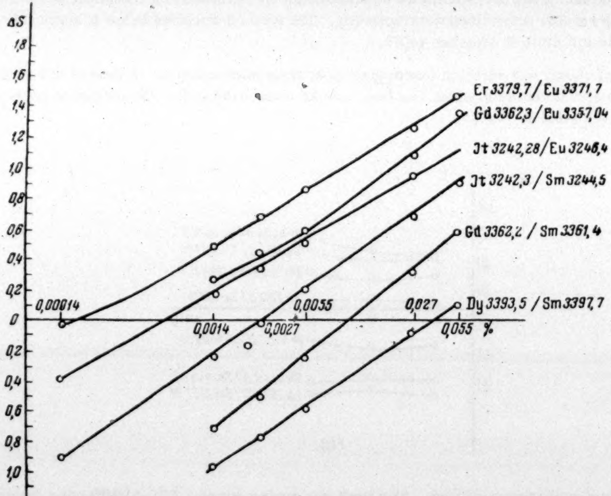
ΔS
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0
0,2
0,4
0,6
0,8
1,0
0,00014
0,0014
0,0027
0,0055
0,027
0,055
%
Er 3379,7 / Eu 3371,7
Gd 3362,3 / Eu 3357,04
Jt 3242,28 / Eu 3246,4
Jt 3242,3 / Sm 3244,5
Gd 3362,2 / Sm 3361,4
Dy 3393,5 / Sm 3397,7

Fig. 3.

Main element	Element determined	Analytical lines*	Concentration determined %
Samarium	Lanthanum	La 4429,9/Sm 4425,8	0,01 —4,0
	Cerium	Ce 4449,34/Sm 4442,58	0,03 —4,0
	Praseodymium	Pr 4408,84 Sm 4408,04	0,03 —4,0
	Neodymium	Nd 4451,57,Sm 4446,37	0,03 —4,0
	Europium	Eu 4435,6/Sm 4433,0	0,008 —5,0
	Gadolinium	Gd 3362,24 Sm 3361,44	0,01 —5,0
	Terbium	Tb 3324,4 Sm 3322,7	0,01 —5,0
	Dysprosium	Dy 3393,58 Sm 3397,79	0,01 —5,0
	Holmium	Ho 3398,98 Sm 3397,79	0,008 —5,0
	Erbium	Er 3372,75 Sm 3372,32	0,002 —5,0
	Ytterbium	Yb 3289,37/Sm 3286,57	0,0002—5,0
	Thullium	Tu 3362,61/Sm 3361,64	0,002 —5,0
	Lutecium	Lu 3397,09 Sm 3397,79	0,01 —5,0
	Yttrium	Y 3242,28,Sm 3244,48	0,001 —5,0
Europium	Lanthanum	La 4429,9/Eu 4438,0	0,1 —4,0
	Cerium	Ce 4449,34 Eu 4446,47	0,3 —4,0
	Praseodymium	Pr 4408,84/Eu 4414,76	0,3 —4,0
	Neodymium	Nd 4451,57 Eu 4446,47	0,3 —4,0
	Samarium	Sm 4433,8 Eu 4438,0	0,01 —4,0
	Gadolinium	Gd 3362,24/Eu 3357,04	0,01 —5,0
	Terbium	Tb 3324,4 Eu 3327,04	0,01 —5,0
	Dysprosium	Dy 3393,58 Eu 3394,03	0,01 —5,0
	Holmium	Ho 3398,98 Eu 3394,03	0,008 —5,0
	Erbium	Er 3379,75 Eu 3371,75	0,002 - 5,0
	Ytterbium	Yb 3289,37 Eu 3288,57	0,0002—5,0
	Thullium	Tu 3362,61 Eu 3357,04	0,002 —5,0
	Lutecium	Lu 3397,07 Eu 3394,03	0,01 —5,0
	Yttrium	Y 3242,28/Eu 3246,44	0,001 —5,0

The internal standard chosen was the rare earth forming the bulk of the test material, since this would make compensation of variations in the excitation conditions even more effective.

The wavelength region used for determination of the cerium group was 4400 A, while for determination of elements of the yttrium group the wavelength region used was 3300-3400 A.

Photographic plates type III with a sensitivity of 4.5 GOST units were used. The developer was Chibisova No. 1.

Preparation of standards. The purest oxides of the rare earths available in the laboratory were used for preparing the standards, after the oxides had been calcined at 900°. Two series of standards were prepared by dissolving the corresponding oxides in HCl.

The first series was a mixture of the elements of the cerium group including europium; the concentrations used were as follows: 0.085, 0.033, 0.0085, 0.0066, 0.0022% La, Ce, Pr, Nd, Sm, Eu.

The second series was a mixture of the elements of the yttrium group including yttrium; the concentrations were as follows: 0.111, 0.055, 0.011, 0.0055, 0.0027, 0.00027; Gd, Dy, Tb, Ho, Er, Tu, Lu, Yb, Y.

Since the internal standard used is the rare earth which forms the bulk of the test material (in our case, samarium and europium), the content of this element should be the same both in test samples and in standards. Accordingly, the series of standards indicated were mixed in the proportion of 1 : 1 (by volume) with a 2% solution of the oxide of samarium oxide during analysis of samarium concentrates, and with a 2% solution of europium oxide during the analysis of europium concentrates.

Preparation of samples. The test samples were dissolved to give solutions with concentrations of 1-10% with respect to samarium and europium.

As tests showed, the optimum concentration is 1-5%. When high concentrations are used, a friable deposit is obtained after evaporation of a drop of the solution; this deposit does not stick very well on the electrode end.

Experiments also showed that the optimum concentration of the salts during dissolution of the test sample is 1%. The standards can be prepared beforehand and stored in test tubes closed with ground-glass stoppers.

Choice of analytical lines. The spectra of the rare earths are extremely complex; accordingly, the most difficult problem in the whole analysis is the choice of the analytical lines.

The analytical pairs of lines chosen were those whose components react in the same way to changes in current strength, interelectrode distance, etc.

The relation between the relative blackenings of the line and the current is shown in Fig. 1.

The analytical lines chosen are given in the table.

The three-standards method was used. Calibration curves were constructed within the coordinates ΔS, $\log C$. Some calibration curves are shown in Figs. 2 and 3.

The correctness of the results was evaluated by introducing known amounts of the test elements, and by comparing the results obtained with the results of x-ray spectrographic analysis, when the content of the impurities did not exceed the sensitivity limit of the x-ray spectrographic method. The agreement between the results obtained by the two methods was fully satisfactory. The error of a single determination was ±3-5% relative.

SUMMARY

A technique has been developed for the quantitative determination of rare earths present as impurities in pure samarium and europium oxides. Determinations can be carried out within the concentration limits 0.01-4%; 0.002-5%. The mean error is 3-5% relative. The minimum amount of test sample required for an analysis is 5-10 mg.

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*See C.B. translation.

PHOTOMETRIC DETERMINATION OF GERMANIUM BY MEANS OF o-DIHYDROXYCHROMENOLS

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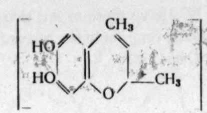
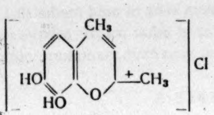
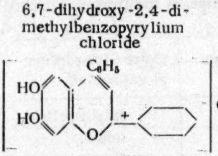
Methods in which colored compounds with organic reagents such as hematin [3], o-dihydroxyazo dyes [4], and phenylfluorone [5] have been used in recent years for the photometric determination of germanium instead of methods based on the formation of germaniomolybdic acid [1] and on its reduction [2]. We have found that benzopyryl or flavyl dyes (chromenols) containing two hydroxy groups in the ortho position in the benzene ring are sensitive reagents for a number of elements, including germanium. It was interesting to find out to what extent these reagents can be used for the photometric determination of germanium. For this purpose, we prepared and studied the following four dihydroxychromenols:


(I)
6,7-dihydroxy-2,4-dimethylbenzopyrylium chloride


(II)
7,8-dihydroxy-2,4-dimethylbenzopyrylium chloride


(III)
6,7-dihydroxy-2,4-diphenylbenzopyrylium chloride

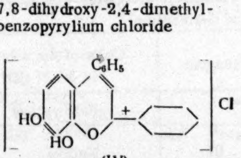

(IV)
7,8-dihydroxy-2,4-diphenylbenzopyrylium chloride

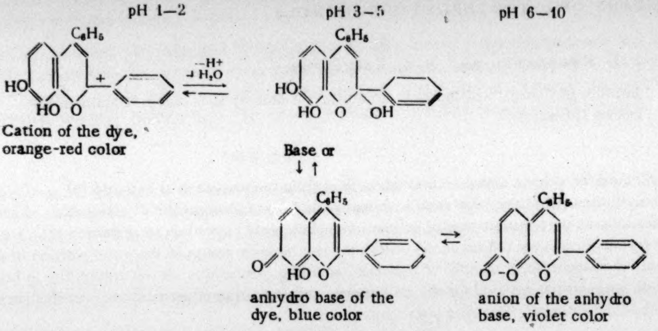
TABLE 1

Colors of Solutions Containing Chromenols as a Function of the pH of the Media

Reagent	Color of the solution at pH 1	2	3	4	5	6	7	8	9	10
I	Pale-yellow	← Lemon yellow →						← Bright-yellow →		
II	Lemon-yellow		← Dark-red →			← Brown-red →				
III	Lemon-yellow	← Red-orange →					← Dark-red →			
IV	Orange-red →		← Blue →			← Violet →				

The chlorides of the dihydroxychromenols are crystalline materials which are yellow, red, or dark brown in color. The salts of the dimethyl derivatives are soluble in water, while the salts of the diphenyl derivatives are insoluble in water, but soluble in alcohol to form brightly colored solutions. The colors of aqueous and aqueous-alcohol solutions change with pH (Table 1).

As is evident from Table 1, the dihydroxychromenols are acid-base indicators, which give three colored forms depending on the pH of the solution. Such behavior on their part can be explained by successive ionization, for example, as follows, in the case of 7,7-dihydroxy-2,4-diphenylbenzopyrylium:



Cation of the dye, orange-red color

anhydro base of the dye, blue color

anion of the anhydro base, violet color

Solutions of germanium salts in acid media (0.1 N HCl) give more or less sharp color changes with the reagents (Table 2). A number of other metals behave similarly; they include: zirconium, hafnium, titanium, thorium, molybdenum, tungsten, vanadium, tantalum, niobium, and tin.

TABLE 2

Changes in the Color of Acid Solutions of the Dyes on Addition of Germanium

Reagent	Color of the solution in 0.1 N HCl	Color with addition of germanium
I	Pale yellow	Bright yellow
II	Orange	Red
III	Yellow	Orange-red
IV	Orange	Dark

The colored germanium complexes of the dimethyl derivatives of the chromenols are soluble in water, while those of the diphenyl derivatives are insoluble and separate out as precipitates; they can, however, be kept in solution by using a protective colloid. In Figs. 1-2 are shown the absorption curves for solutions of the reagents (curves 1 and 3) and of solutions of their compounds with germanium (curves 2 and 4). As is evident from these curves, during complex formation with germanium, there is observed a bathochromic shift of the absorption bands of the dye and an expansion of these bands.

Conditions for the photometric determination of germanium in solution by means of dihydroxychromenols. Each of the reagents synthesized was examined with the object of establishing the optimum wavelength at which germanium should be determined, the effect of hydrochloric acid concentration on the optical density of the solution, the stability of the color with time, the optimum amounts of reagent and protective colloid (gelatin), the sensitivity of the method, the germanium concentration range for which the determination can be carried out, and whether or not Beer's law is obeyed.

As the results in Table 3 show, the reagent which proved to be most sensitive and gave the most contrasting color change was 6,7-dihydroxy-2,4-diphenylbenzopyranol. The optical density can be measured both on

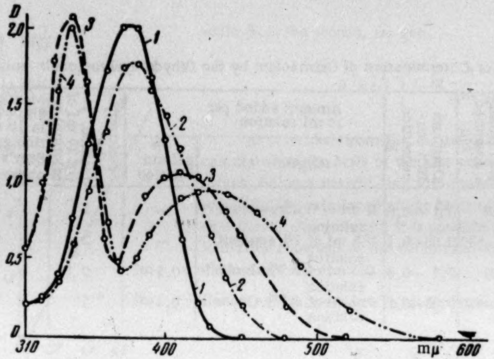


Fig. 1. Absorption curves for solutions of 6,7-dihydroxydimethylbenzopyrylium chloride (1), and of its compound with germanium (2); absorption curves for solutions of 7,8-dihydroxy-2,4-dimethylbenzopyrylium chloride (3), and of its compound with germanium (4).

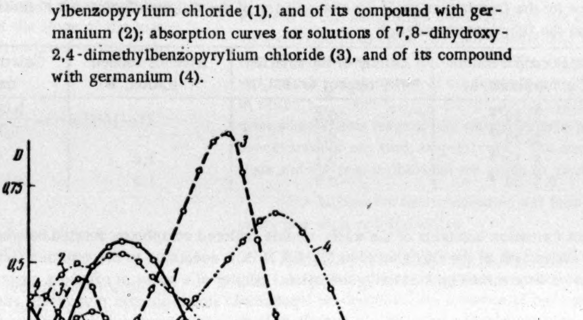


Fig. 2. Absorption curves for solutions of 7,8-dihydroxy-2,4-diphenylbenzopyrylium chloride (1), and of its compound with germanium (2); absorption curves for solutions of 6,7-dihydroxy-2,4-diphenylbenzopyrylium chloride (3), and of its compound with germanium (4).

the SF-4 spectrophotometer, and on the FM-1 photometer or the FÉK-M photoelectrocolorimeter, using a cuvette with a layer thickness of 5 mm (the 6,7-dihydroxyphenyl derivative) and 10 mm (the other reagents).

The color develops immediately on addition of reagents I and II, and reaches a maximum in 3-5 minutes in the case of reagents III and IV; the color subsequently remains constant for 24 hours.

Composition and formation constants of the colored germanium complexes. The composition of the compounds formed between germanium and the tested dihydroxychromenols was studied in each case by the isomolar series method of Ostromyslenskii-Job, by determining the optical density of the solutions at the wavelengths given in Table 3. The experimental conditions used are given in Table 4.

The results obtained (Fig. 3) show that germanium forms compounds with all the reagents in which there are two molecules of reagent for one atom of germanium.

TABLE 3

Conditions for Determination of Germanium by the Dihydroxychromenols Studied

Re-agent	Wavelength at which optical density is measured, mμ	Optimum HCl concentration, N	Amount added per 10 ml solution		Sensitivity of the method, γ (in 10 ml of solution)	Maximum amount Ge (γ) in 10 ml solution at which Beer's law is obeyed
			reagent	1% gelatin solution		
I	420	0.1 —0,6	2 ml of 0.2% aqueous solution	—	1	100
II	500—530	0.05—0,2	0.5 ml of 1% aqueous solution	—	2	100
III	500	0.1 —0,6	0.5 ml of 0.2% alcoholic solution	0,5 ml	0.1	25
IV	600—630	0.05—0,2	0.5 ml of 0.2% alcoholic solution	0,5 ml	1	40

TABLE 4

Conditions Used for the Determination of the Composition of the Colored Compounds Formed Between Germanium and the Dihydroxychromenols

Reagent	Total concentration of components, M	Acidity of the solution with respect to HCl, N	Alcohol concentration, %	Gelatin concentration, %
I	$2 \cdot 10^{-2}$	0.5	—	—
II	$2 \cdot 10^{-2}$	0.1	—	—
III	$2 \cdot 10^{-3}$	0.1	1.0	0.04
IV	$2.5 \cdot 10^{-3}$	0.2	1.0	0.04

The apparent formation constants of the water-soluble, colored complexes, formed between germanium and the dimethyl derivatives of the chromenols in 0.1-0.2 N HCl, according to the equation $GeO_2 + 2HA \rightleftharpoons GeOA_2 + H_2O$, were determined by measuring the optical density of a series of solutions containing the components in stoichiometric proportion, and in solutions where the concentration of reagent was in excess, so that dissociation of the complexes was suppressed. The colored colloidal solutions of the complexes formed with the diphenyl derivatives in the presence of gelatin also conform to the law of mass action in a certain concentration range, and the equations for the formation of the colored soluble complexes are applicable to them. This follows from the fact that on determining the composition of these complexes on the basis of the slope of the logarithmic curves, correct results are obtained on using the equation

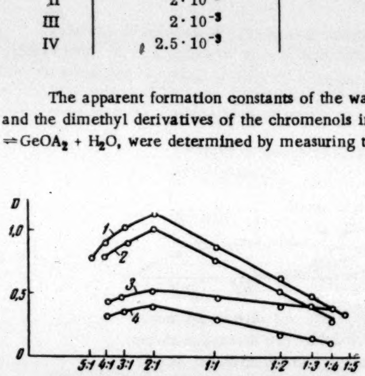


Fig. 3. Composition of the colored compounds formed between germanium and the dihydroxychloromenols: 1) 7,8-dihydroxy-2,4-dimethylbenzopyrylium chloride; 2) 7,8-dihydroxy-2,4-diphenylbenzopyrylium; 3) 6,7-dihydroxy-2,4-dimethylbenzopyrylium chloride; 4) 6,7dihydroxy-2,4-diphenylbenzopyrylium.

$$\frac{[GeO^{2+}][A^-]^n}{[GeOA_2]} = K'_{\text{dissoc.}}$$

and not the equation

$$[GeO^{2+}][A^-]^n = L_{\text{sol.}}$$

Transforming these equations, and replacing the concentrations of the ions by the concentrations of the components which are proportional to them, we get from the first equation:

$$n \lg [HA] = \lg \frac{[GeOA_2]}{[GeO_2]} + \text{const},$$

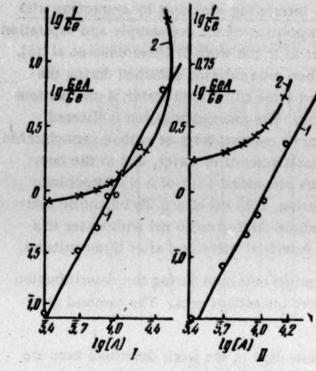


Fig. 4. Composition of the complexes by the method of the slope of the logarithmic curves calculated on the basis of the equations

$$\lg\frac{[GeOA_2]}{[GeO_2]} = n\lg[HA] - (1)$$

for the solutions and

$$\lg\frac{1}{[GeO_2]} = n\lg[A^-] - (2)$$

for formation of precipitates I with 6,7-dihydroxy-2,4-diphenylbenzopyrylium; II with 7,8-dihydroxy-2,4-diphenylbenzopyrylium.

while from the second, we get:

$$n\lg[A^-] = \lg\frac{1}{[GeO_2]} + \text{const}.$$

As is evident from Fig. 4, the values for $\log[GeOA_2]/[GeO_2]$, calculated on the basis of the first equation for the soluble complexes, lie on a straight line with $\tan\alpha = 2$, while the values of $\log 1/[GeO_2]$, calculated on the basis of the second equation, lie on a curve. Accordingly, it is possible to calculate the apparent formation constants of the complexes with the diphenyl derivatives of the chromenols.

Calculations were made by means of the formula

$$K'_{\text{formation}} = \frac{(1-\alpha)}{4\alpha^3C^3} = \frac{1}{K'_{\text{dissoc.}}}$$

where α is the percentage dissociation of the complex for stoichiometric concentrations of the components, and C is the concentration of germanium ions in solution. The degree of dissociation α was calculated by means of the formula $\alpha = (E_{\text{max}} - E_{\text{stoich}})/E_{\text{max}}$, in which E_{max} and E_{stoich} are the optical densities of the solutions when excess reagent and stoichiometric proportions of the concentrations are used, respectively. The experimental conditions and the results obtained are given in Table 5.

The highest formation constant was found for the 6,7-dihydroxy-2,4-diphenyl derivative.

Masking of foreign metals in the reaction with the chromenols. A number of masking agents were tested for simplifying the analytical procedure in the presence of not very large amounts of foreign elements. The most suitable masking agent proved to be a mixture of sodium ethylenediaminetetracetate, hydrogen peroxide, and phosphoric acid. Sodium ethylenediaminetetracetate masks zirconium, hafnium, thorium, iron (III), tin (IV), and bismuth; phosphoric acid masks titanium, while hydrogen peroxide decreases the effect of molybdenum, tungsten, antimony, and vanadium. In the presence of the amounts of the masking agents indicated below, the following amounts of the listed elements can be present in 25 ml of solution: up to 12.5 mg bismuth, 2.5 mg thorium, 1.5 mg iron (III), 1.0 mg titanium, 0.75 mg aluminum, 0.5 mg zirconium, or 1 mg hafnium, 0.4 mg tin (IV), 100 γ vanadium, 40 γ niobium, 30 γ tantalum, 20 γ tin (IV), 15 γ tungsten, 5 γ molybdenum, and 5 γ antimony. The intensity of the color of the germanium complex does not alter appreciably under these conditions. These masking agents can also be used for the determination of germanium by means of phenylfluorone and other similar reagents.

Experimental procedure. a) In the presence of small amounts of foreign elements, without preliminary separation. A known amount of test solution is pipetted into a 25 ml standard flask, and 1 ml of 5 N HCl, 0.2 to 0.3 ml of phosphoric acid (1 : 1), 2-3 drops of hydrogen peroxide, and 2 ml of a 5% solution of sodium ethylenediaminetetracetate added in succession with stirring; 1 ml of a 1% solution of gelatin and 1.25 ml of a 0.2% ethanolic solution of the reagent (6,7-dihydroxy-2,4-diphenylbenzopyranol) are then added. The final solution is diluted with distilled water to the mark, and after three minutes the optical density is measured relative to the solution from the control test on a SF-4 spectrophotometer in 20 mm cuvettes at 500 $m\mu$. The germanium content is determined by means of a calibration curve. The calibration curve is linear up to concentrations of 25 γ of germanium in solution (Fig. 5).

Table 6 contains the results of determination of germanium in synthetic mixtures.

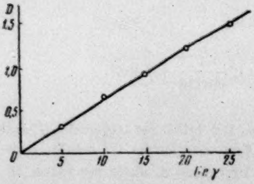
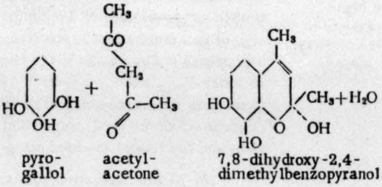


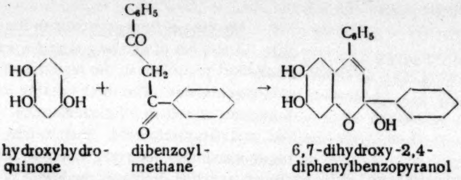
Fig. 5. Calibration curve for the spectrophotometric determination of germanium by means of 6,7-dihydroxy-2,4-diphenylbenzopyrylinium chloride.

b) After removal from interfering elements by extraction with carbon tetrachloride. Decomposition of the ore sample and separation of germanium are carried out as in the work of Nazarenko et al [5]. The solution of $GeCl_4$ in carbon tetrachloride obtained during the analytical process is extracted three times with water, 4-ml portions of water being used each time. The aqueous solution is filtered through a small filter in order to remove drops of carbon tetrachloride, the filter is washed with a small amount of water, and to the combined filtrate and wash liquors are added 1 ml of 5 N hydrochloric acid, 1 ml of 1% gelatin solution, 1.25 ml of a 0.2% ethanolic solution of the reagent, and the whole diluted to 25 ml with water in a standard flask. The optical density is measured after three minutes.

Table 7 contains the results obtained during the determination of germanium in silicate rocks and sulfide ores. The method gives satisfactory results.

Synthesis of the dihydroxychromenols [6]. The dihydroxychromenols used in the work described here are readily prepared by the condensation of 1,3-diketones with trifunctional phenols:


CH₃
CO
CH₂
C—CH₃
O
HO
OH
OH
+
CH₃
HO
CH₃+H₂O
O
OH
HO
pyrogallol
acetylacetone
7,8-dihydroxy-2,4-dimethylbenzopyranol


C₆H₅
CO
CH₂
C—
O
HO
HO
OH
+
→
C₆H₅
HO
HO
O
OH
hydroxyhydroquinone
dibenzoylmethane
6,7-dihydroxy-2,4-diphenylbenzopyranol

As an example, we shall describe the synthesis of 6,7-dihydroxy-2,4-diphenylbenzopyranol [7].

TABLE 5

Experimental Conditions and Results of the Determination of the Apparent Formation Constants and Molar Extinction Coefficients of the Germanium Complexes with Dihydroxychromenols

Reagent	Ge concentration, M	HCl concentration, N	Thickness of layer in cuvette, mm	Values found		α		Molar extinction coefficient
				$E_{stoich.}$	E_{max}			
I	$2\cdot10^{-4}$	0,1	10	0,51	1,1	0,536	$1,9\cdot10^{7}$	5 500
	$1,6\cdot10^{-3}$	0,1	10	0,56	0,75	0,252	$0,5\cdot10^{7}$	4 700
II	$2\cdot10^{-4}$	0,1	10	0,075	0,585	0,87	$1,3\cdot10^{7}$	2 925
III	$1\cdot10^{-4}$	0,1	5	0,74	1,1	0,326	$4,8\cdot10^{8}$	25 000
IV	$1\cdot10^{-4}$	0,2	5	0,275	0,78	0,52	$0,8\cdot10^{8}$	15 600

TABLE 6

Determination of Germanium in Mixtures of Cations Without Preliminary Separation

Ge taken, γ	Added														Ge found, γ	Difference, γ
	Fe(III), mg	Al, mg	Bi, mg	Ti, mg	Hf, mg	Zr, mg	Th, mg	Ta, γ	Nb, γ	Sb(III), γ	V, γ	Mo, γ	Sn(IV), γ	W, γ		
1	1	0,5	5	0,5	—	—	—	20	—	—	—	5	—	—	1	0,0
2,5	1	0,75	—	—	—	0,2	1	—	—	—	—	—	—	—	3	+0,5
2,5	—	—	—	—	—	—	—	20	—	—	50	5	—	10	2,4	−0,1
5	1	0,5	5	—	1	—	—	20	20	4	—	—	—	—	5,6	+0,6
5	1	0,5	2	—	—	—	1	—	—	—	—	—	15	—	5,0	0,0
10	1	0,75	—	—	—	0,25	1	—	—	—	—	—	—	—	10,4	+0,4
10	—	—	—	—	—	—	—	20	—	—	50	5	—	10	10,3	+0,3
12	1	0,5	—	0,2	—	—	—	20	—	—	50	5	—	—	12,6	+0,6
18	1,5	0,75	—	0,5	—	—	1	—	—	4	—	—	—	15	17,9	−0,1
20	1	0,5	5	0,2	—	—	—	20	—	4	70	5	—	—	20	0,0

TABLE 7

Determination of Germanium in Rocks and Ores

Test material	Ge added, %	Ge found, together with added germanium%	Difference, %
Silicate rock (sample	—	0,00058	
No. 1)	0,0005	0,00105	−0,00003
Silicate rock (sample	—	0,00038	
No. 2)	0,001	0,00136	−0,00002
Silicate rock (sample	—	0,00095	
No. 3)	0,0007	0,00161	−0,00004
Sulfide-zinc ore	—	0,00029	
(sample No. 1)	0,0008	0,00109	0,000
Sulfide-zinc ore	—	0,00078	
(sample No. 2)	0,0005	0,00128	0,000
Pyrites	0,001	0,00012	
		0,0011	−0,00002

0.6 g of pyrogallol A (triacetylhydroxyhydroquinone) is dissolved in 4 ml of glacial acetic acid and a stream of dry hydrogen chloride passed through the solution for half an hour; 0.6 g of dibenzoylmethane is added and hydrogen chloride passed through for a further 4-5 hours. The flask is then tightly sealed and allowed to stand for 24 hours. A crystalline, yellow-orange precipitate separates out. The mixture is cooled in ice for an hour and the preparation which separates out is filtered off and washed with ether. In order to purify the product, a saturated solution of it is prepared in alcohol by heating, the solution is filtered and an equal volume of concentrated hydrochloric acid is added. The chromenol chloride which separates out on cooling and on rubbing with a rod is filtered off, and washed with a 1% solution of hydrochloric acid; it is finally dried in air.

SUMMARY

A study has been made of the behavior of germanium toward four representatives of the group of o-dihydroxybenzopiperyl dyes (dihydroxy chromenols). 6,7-Dihydroxy-2,4-diphenylbenzopiperylium chloride gives the most sensitive reaction; in acid media (0.1 N HCl) the color changes from yellow to orange-red. This reagent permits determination of 0.1-25 γ of germanium in 10 ml of solution. A technique has been developed for the determination of germanium in various materials. It has been established that the ratio between the number of molecules of reagent and the number of atoms of germanium in the colored complexes formed is 2 : 1; the apparent formation constants of the complexes have been determined.

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*See English translation.

COMPLEXONOMETRIC DETERMINATION OF ZIRCONIUM

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Methods for the complexonometric determination of zirconium are based on direct titration of zirconium with sodium ethylenediaminetetracetate (EDTA-Na) in the presence of the appropriate metal indicator [1-6], and on the back titration of excess EDTA-Na with some salt [7-13]. The most interesting method for the direct titration of zirconium with EDTA-Na is the method using p-nitrobenzeneazopyrocatechol as indicator, first suggested by N.S. Poluéktov et al [5]. Titration is carried out in a medium of 2 N HCl which determines the high selectivity of the method, since under these conditions all the other metals (with the exception of Hf) do not react with EDTA. The drawback of this method, which is also inherent in other methods based on direct titration of zirconium, is the indistinct change in the color at the equivalence point. This apparently is determined not so much by the properties of the indicators used, but by the very process of complex formation between zirconium and EDTA-Na.

Titration of zirconium with EDTA-Na is usually carried out in a hot solution, while it is often recommended that the solution be boiled again near the equivalence point and up to the end of the titration. But, under these conditions, the reaction does not go to completion, and a direct proportionality between the amount of EDTA-Na solution used for titration and the amount of zirconium is not observed. When the theoretical amount of EDTA-Na with respect to zirconium is used (1 ml of 0.1 EDTA-Na is equivalent to 9.122 mg Zr) the results are usually 4-5% (relative) low [6]. Accordingly, in practical work, an empirical titer is used for zirconium, which is established by titrating a known amount of zirconium with EDTA-Na.

Direct-titration methods give satisfactory results when zirconium is determined in comparatively pure solutions; for example, in solutions of zirconium sulfate and oxychloride free from large amounts of other elements. Extension of these methods to more complex mixtures obtained during the analysis of ores, concentrates, cakes, and other products often does not yield satisfactory results; this led us to use the back-titration method.

When the back-titration technique is used, more consistent results can be obtained by boiling the solution of the zirconium salt with EDTA-Na, taken in excess, in a medium of 2 N HCl. Under such conditions, the interaction of zirconium with EDTA-Na proceeds to completion; in this way, the basic cause for the error in direct titration is eliminated. Existing methods of back titration did not satisfy us for a variety of reasons. Back titration with bismuth nitrate [12] is inconvenient for mass determinations, since, in order to obtain reproducible results, the pH of the medium must be accurately maintained (pH 2). This is only possible by using a pH-meter, while for amperometric determination of the equivalence point [13] a polarographic setup is required.

Back titration of excess EDTA-Na with a ferric salt using salicylic, sulfosalicylic acids [9-11], or potassium benzohydroxamate [7, 8] as indicators is widely used abroad. But, since the titration is carried out at pH 4-6, where many other elements also form stable complexonates, such elements have to be removed beforehand.

Moreover, the drawback of the direct-titration method is also inherent in these methods; namely, as a rule, the introduction of EDTA-Na into the test zirconium solution is carried out at room temperature while the pH of the medium is usually not less than 1. Accordingly, here again, interaction of zirconium with EDTA-Na is not complete, this being the main source of error during the determination. Taking all these facts into account, we decided to concentrate on that variant of the back-titration method which ensures that the reaction with EDTA-Na proceeds to completion. For this purpose, the EDTA-Na is introduced into a boiling solution of zirconium (2 N HCl), and the solution boiled for a few more minutes. Under these conditions, the zirconium is selectively and completely bound as its complexonate. Excess EDTA-Na is titrated with a solution of thorium nitrate.

Thus, determination of zirconium in various materials consists of the following stages: an aliquot of test material is brought into solution by fusing it with potassium bifluoride, with subsequent treatment of the melt with sulfuric acid; zirconium hydroxide is precipitated from the sulfuric acid solution with ammonia, and is dissolved in hot 2 N HCl. To the boiling hydrochloric acid solution of zirconium is added a measured excess of a standard EDTA-Na solution; the solution is boiled for several minutes and then cooled to room temperature; it is neutralized to pH 2.3-2.5, and excess EDTA-Na titrated with a solution of thorium nitrate using arsenazo, also called uranon* [14, 15], as indicator. The optimum amounts of zirconium for a determination are 5-80 mg. The effect of foreign elements on zirconium determination can be seen from the results given in Table 1.

TABLE 1

Effect of Foreign Elements on the Complexonometric Determination of Zirconium
(15.37 mg Zr was used in the first 15 experiments, and 15.59 mg Zr in the remainder)

Impurity introduced, mg	Zr found, mg	Error, %		Impurity introduced mg	Zr found, mg	Error, %	
		abs.	rel.			abs.	rel.
30 Zn^{2+}	15,37	0,0	0,0	50 UO_2^{2+}	15,37	0,0	0,0
500 Zn^{2+}	15,37*	0,0	0,0	500 WO_4^{2-}	15,37*	0,0	0,0
500 Zn^{2+}	15,37**	0,0	0,0	500 MoO_4^{2-}	15,28*	–0,09	–0,6
200 Cu^{2+}	15,46	+0,09	+0,6	200 VO_3^-	15,46*	+0,09	+0,6
500 Cu^{2+}	15,37**	0,0	0,0	5 Fe^{3+}	15,59	0,0	0,0
5 Ni^{2+}	15,28	–0,09	–0,6	3 Ti^{IV}	15,59	0,0	0,0
200 Ni^{2+}	15,46**	+0,09	+0,6	15 Ti^{IV}	15,69***	+0,1	+0,6
15 Co^{2+}	15,37	0,0	0,0	100 Ce^{3+}	15,69	+0,1	+0,6
200 Co^{2+}	15,41**	+0,04	+0,25	200 La^{3+}	15,69	+0,1	+0,6
500 Al^{3+}	15,41*	+0,04	+0,25	200 Nd^{3+}	15,69	0,0	0,0
150 Mn^{2+}	15,37	0,0	0,0				

Note. After precipitation of zirconium with sodium hydroxide (*), ammonia (**), and ammonia in the presence of hydrogen peroxide (***).

TABLE 2

Complexonometric and Gravimetric Phosphate Determinations of Zirconium

Test material	Zr found by complexonometric method	Mean value of Zr, %	Zr found by phosphate method, % (mean of three determinations)	Deviation, abs., %
Ore concentrate	38,47; 38,49; 38,76	38,57	38,62	–0,05
Cake	12,17; 12,29; 12,17; 12,17	12,20	12,29	–0,09
»	17,16; 17,28; 17,32	17,25	17,10	+0,15
»	4,26; 4,26; 4,26	4,26	4,28	–0,02
»	18,20; 18,02; 18,02	18,08	18,21	–0,13
»	10,47; 10,47; 10,47	10,47	10,36	+0,11
»	2,68; 2,68; 2,68	2,68	2,67	+0,01
»	2,80; 2,68; 2,68	2,72	2,76	–0,04
	13,03; 13,03	13,03	12,96	+0,07
	7,07; 7,07	7,07	7,18	–0,11
	1,83; 1,83; 1,85	1,84	1,85	–0,01

Th^{4+}, Bi^{3+}, PO_4^{3-}, F^-, and the anions of oxalic, tartaric, citric, and other acids interfere with the determination in all cases.

Comparison of the results obtained by the titrimetric method and by a gravimetric phosphate method indicates that good agreement is obtained between them (Table 2).

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*Xylenol orange can also be used as an indicator.

Analytical procedure. 0.1-0.2 g of test material, depending on the expected zirconium content, is fused in a platinum basin with 1-3 g of potassium bifluoride in a muffle until a transparent melt is obtained. On cooling, 15-20 ml of concentrated H_2SO_4 is added to the melt, and the mixture evaporated on a sand bath until copious sulfuric acid fumes are evolved.

On cooling, the sulfuric acid solution is transferred from the basin into a 300 ml beaker, and, depending on the composition of the test material, zirconium is separated by one of the known methods.

a) Determination of Zirconium in the Presence of Zn^{2+}, Al^{3+}, Fe^{3+}, Sn^{2+}, Sn^{4+}, VO_3^-, Cr_4^{2-}, MoO_4^{2-}, WO_4^{2-}, PO_4^{3-}

To the sulfuric acid solution of zirconium is added, in the cold, a 20% solution of sodium hydroxide until the zirconium hydroxide has been precipitated completely; 5-10 ml of the sodium hydroxide solution is then added in excess. The volume of the solution plus precipitate should not be less than 200 ml. The precipitate is filtered off through not too fine a filter paper (white band) and washed 6-8 times with 5% sodium hydroxide solution. The washed precipitate is washed off the filter paper with a hot 2 N solution of hydrochloric acid into the beaker in which the precipitation was effected and is heated until it dissolves completely (the volume of the solution should not exceed 100 ml). The solution is boiled for 2-3 minutes and ascorbic acid added to reduce Fe^{3+}; 0.05 M EDTA-Na solution is pipetted into the boiling solution. The solution is boiled for 2-3 minutes and then cooled to room temperature, 1-2 drops of a 1% alcoholic solution of α-dinitrophenol is added and the solution neutralized with ammonia until it has a bright-yellow color; hydrochloric acid (1:2) is then added dropwise, until the color disappears (pH 2.3-2.4). Six to eight drops of a 0.1% aqueous solution of uranon (or 2-3 drops of a 0.5% solution of xylenol orange) is added, and excess EDTA-Na back titrated with a solution of thorium nitrate until the color changes from bright rose to blue-violet.

b) Determination of Zirconium in the Presence of Zn^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} (T_1^{4+} not more than 15 mg) and in the Absence of PO_4^{3-}

This method can also be used for the analysis of such materials as copper-zirconium ligatures.

To the original sulfuric acid solution is added 1.5-3 ml of 30% H_2O_2 and (in the cold) a 25% ammonia solution, until the zirconium hydroxide has been completely precipitated; 3-5 ml of the ammonia solution is then added in excess (the volume of the solution should not be less than 250 ml). The precipitate is filtered through not too fine a filter paper (white band) and washed 6-8 times with a cold 2% solution of NH_4Cl containing a small amount of ammonia and H_2O_2. The precipitate is washed off the filter with hot 2 N hydrochloric acid into the beaker in which the precipitation was carried out, and the procedure outlined above then followed.

A single determination does not take more than 1-1.5 hours, without taking into account the time taken to decompose the test material.

SUMMARY

A complexonometric method is suggested for the determination of zirconium; it consists of the following stages. The test material (ores, concentrates, cakes, alloys, etc.) is decomposed by a suitable method, and the zirconium is precipitated with ammonia or sodium hydroxide, the precipitate is dissolved in 2 N HCl and is boiled with excess EDTA-Na, the pH of the solution is then adjusted to 2.3-2.4, and excess EDTA-Na is back titrated with thorium nitrate using uranon (arsenazo) or xylenol orange as indicator.

The experimental error does not exceed ±0.6% (relative).

The method has been used for the determination of zirconium in ores, cakes, and concentrates containing from 2 to 40% of zirconium, and gave satisfactory results.

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THE SOLUBILITY OF ZIRCONIUM CUPFERRONATE

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Cupferron (ammonium nitrosophenylhydroxylamate) finds wide application in the analytical chemistry of zirconium. The first determination of zirconium by means of cupferron was carried out by Schroder [1]. Later, cupferron was used by other authors [2] for removing impurities from zirconium. Cupferron can be used for separating zirconium from Al^{3+}, Mg^{2+}, Be^{2+}, Zn^{2+}, UO_2^{2+} and other elements which are not precipitated by this reagent in an acid medium. That such a separation is possible depends on the completeness of precipitation of zirconium with excess cupferron in the medium selected. Accordingly, a study of the solubility of zirconium cupferronate as compared with the solubility of the cupferronates of the elements which we were interested in is of considerable importance.

Zirconium forms a white, bulky precipitate of $Zr(C_6H_5NNOO)_4$ [1] with cupferron. Precipitation is quantitative even in 4 N sulfuric acid or in 6 N hydrochloric acid. Until recently, no accurate data were available on the solubility of zirconium cupferronate. Pinkus and Martini [3] have studied the solubility of the cupferronates of a series of metals. The method which they developed consisted of shaking the metal cupferronate with water until saturation was reached at a constant temperature; this method, however, could not be used for zirconium cupferronate because of the large tendency of zirconium to hydrolyze. Moreover, values of the solubility of the cupferronates which are not determined under the conditions in which the metals are precipitated and separated by means of cupferron, cannot serve as a criterion for the quantitative precipitation of the cupferronates.

Pyatnitskii [4] suggested a new method for the determination of the solubility of metal cupferronates. The method consists in determining the equilibrium constants of the reaction between the metals and cupferron in an acid medium, i.e., under conditions approximating to those used for precipitation of the metals by cupferron. From the equilibrium constants of the reactions the solubility product (L_s), and hence, the solubility of the metal cupferronate, are determined. In its application to zirconium, Pyatnitskii's method has a number of advantages over other methods; we used it for determining the solubility of zirconium cupferronate.

The equilibrium constant is readily found by means of the following simple equations:

$$Me^{4+} + 4HR \rightleftarrows MeR_4 + 4H^+. \quad (1)$$

$$K_{eq} = [H^+]^4/[Me^{4+}][HR]^4. \quad (2)$$

The solubility product L_s for MeR_4 can be expressed by the formula:

$$L_s = [Me^{4+}][R^-]^4. \quad (3)$$

The dissociation constant of nitrosophenylhydroxylamic acid is equal to

$$K_S = [H^+][R^-]/[HR]. \quad (4)$$

Substituting the value of $[H^+]$ from Eq. (4) in Eq. (2), we get

$$L_s = K_S^4/K_{eq} \quad (5)$$

Equation (5) gives the possibility of calculating the value of the solubility product of the metal cupferronate, as long as the equilibrium constant of the reaction is determined ($K_{eq.reaction}$). The value of the dissociation constant of nitrosophenylhydroxylamine determined by Pyatnitskii, and which proved to be $5.3 \cdot 10^{-5}$, was substituted in the equation.

The method used for determining the solubility consisted of the following. Into a 100-ml beaker placed in a thermostat maintained at 20° was introduced an accurate amount of zirconium in the form of a 1 M sulfuric acid solution, the acidity of the solution was then accurately adjusted with respect to sulfuric acid, taking into account the amount of aqueous cupferron solution added. The ionic strength of the solutions in each case was adjusted to 2 by means of ammonium sulfate. Solubility determinations were carried out in a sulfuric acid medium (not in perchloric acid solutions, which prevent complex formation), because of the fact that, during the analysis of zirconium for impurities, sulfuric acid solutions are obtained in bringing the test material into solution. Zirconium was precipitated by adding, from a buret, a known volume of a freshly prepared standard aqueous solution of cupferron, taken in excess as compared with the stoichiometric amount. The solution and precipitate were stirred for 2-3 minutes, and the precipitate filtered through a No. 4 glass filter. The concentration of the zirconium in the filtrate was determined by the method of labeled atoms, using Zr^{95} (purified from radioactive Nb^{95}) as radioactive indicator.

The γ-activity of the filtrates was measured on a γ-scintillation setup and was expressed in terms of the relative values of the number of impulses per minute with a reproducibility of the order of ±5% (relative). 5 and 10 mg of zirconium were taken for the experiments. $4.115 \cdot 10^5$ impulses/minute corresponded to one milligram of zirconium. However, it was impossible to use the value of the total concentration of zirconium in solution for calculating the equilibrium constant. Zirconium compounds hydrolyze strongly in aqueous solutions. Zirconium forms a considerable number of complex ions, particularly in sulfuric acid media; zirconium also has a tendency to form polymeric compounds. Depending on the hydrogen-ion concentration, in aqueous solutions, the following equilibrium is established:

$$Zr^{4+} + n\,H_2O \rightleftarrows Zr(OH)_n^{4-n} + n\,H^+. \tag{6}$$

consequently, in addition to quadrivalent Zr^{4+} ions, tri-, di-, and uni-charged complex ions will be present in solution, and, accordingly, must be taken into account in calculating the equilibrium constants ($K_{eq.}$) of the reaction.

Connick and McVey [5] in their study of complex formation of zirconium with sulfate ions, adduce the following formation constants for the complexes:

$$Zr^{4+} + HSO_4^- = ZrSO_4^{2+} + H^+;\; K_1 = \frac{[ZrSO_4^{2+}][H^+]}{[Zr^{4+}][HSO_4^-]} = 4{,}6 \cdot 10^2; \tag{7}$$

$$ZrSO_4^{2+} + HSO_4^- = Zr(SO_4)_2 + H^+;\quad K_2 = \frac{[Zr(SO_4)]_2[H^+]}{[ZrSO_4^{2+}][HSO_4^-]} = 53; \tag{8}$$

$$Zr(SO_4)_2 + HSO_4^- = Zr(SO_4)_3^{2-} + H^+;\; K_3 = \frac{[Zr(SO_4)_3^{2-}][H^+]}{[Zr(SO_4)_2[HSO_4^-]} = 1. \tag{9}$$

Solovkin [6], during a study of the extraction of micro amounts of zirconium by tributylphosphate as a function of hydrogen-ion concentration and nitrate-ion concentration, determined the constants for the successive hydrolysis reactions of Zr^{4+}, and at an ionic strength of the solution of 2 these proved to be

$$Zr^{4+} + H_2O = Zr(OH)^{3+} + H^+;\; K_4 = \frac{[Zr(OH)^{3+}][H^+]}{[Zr^{4+}]} = 0{,}6; \tag{10}$$

$$Zr(OH)^{3+} + H_2O = Zr(OH)_2^{2+} + H^+;\; K_5 = \frac{[Zr(OH)_2^{2+}[H^+]}{[Zr(OH)^{3+}]} = 0{,}24; \tag{11}$$

$$Zr(OH)_2^{2+} + H_2O = Zr(OH)_3^{+} + H^+;\; K_6 = \frac{[Zr(OH)_3^{+}][H^+]}{[Zr(OH)_2^{2+}]} = 0{,}09. \tag{12}$$

No quantitative characteristic for the formation of polymeric ions in sulfuric acid solutions is available. Connick and Reas [7] studied the polymerization of zirconium in 1 and 2 M perchloric acid solutions, and showed that polymerization occurs at comparatively high zirconium concentrations (10^{-3} to 10^{-4} mole/liter). At lower concentrations and higher acidity zirconium is found in the form of the quadri-charged monomer. Under the conditions we used in our work, in which the zirconium concentration is less than 10^{-3} mole/liter, polymerization cannot play an important role, and, compared with the corrections which have to be applied for complex formation and hydrolysis, its effect can be disregarded. Thus, the total concentration in solution C_{Zr} will be given by:

$$C_{Zr} = Zr^{4+} + ZrSO_4^{2+} + Zr(SO_4)_2 + Zr(SO_4)_3^{2-} + Zr(OH)^{3+} + Zr(OH)_2^{2+} + Zr(OH)_3^{+}. \tag{13}$$

Substituting in Eq. (13) the value of each component found from Eqs. (7)-(12), we get:

$$C_{Zr} = Zr^{4+} + \frac{K_1[HSO_4^-][Zr^{4+}]}{h} + \frac{K_1K_2[HSO_4^-]^2[Zr^{4+}]}{h^2} + \frac{K_1K_2K_3[HSO_4^-]^3[Zr^{4+}]}{h^3} + \frac{K_4K_5[Zr^{4+}]}{h^2} + \frac{K_4K_5K_6[Zr^{4+}]}{h^3}. \tag{14}$$

After the usual transformations we find the value of Zr^{4+}:

$$Zr^{4+} = \frac{C_{Zr}h^3}{h^3 + K_1[HSO_4^-]h^2 + K_1K_2[HSO_4^-]^2h + K_1K_2K_3[HSO_4^-]^3 + K_4h_2 + K_4K_5h + K_4K_5K_6}. \tag{15}$$

The concentration of hydrogen ions and HSO_4^- ions is calculated in each case on the basis of the formula and Luter's tables [8], in accordance with the accurately measured amounts of sulfuric acid introduced into the solutions (columns 7 and 8, Table 1). On the basis of the total concentration of zirconium found in the filtrate, the ionic concentration $[Zr^{4+}]$ in each of the experiments carried out was calculated by means of formula (15).

Knowing the original amount of zirconium and cupferron, the zirconium content of the filtrate, and the acidity of the original solution, the equilibrium concentrations of nitrosophenylhydroxylamine were calculated, assuming that the latter is found in the form of the undissociated molecule. From the equilibrium concentrations $[H^+]$, $[Zr^{4+}]$, and [HR], the equilibrium constants of the reaction ($K_{eq.}$) were calculated, and, using formula (5), the solubility product (L_s) calculated. The experimental results and the calculated values are given in the table.

Determination of $K_{eq.}$ for Precipitation of Zirconium by Cupferron. Volume of Filtrate 50 ml

Zirconium taken, mg	Cupferron introduced, mg	H_2SO_4 concentration, mole/liter	Zirconium determined in filtrate			Equilibrium concentrations, mole/liter, $K_s = 3.36 \cdot 10^{19}$				$K_s \cdot 10^{19}$
			aliquot, ml	imp/min in the aliquot	total, mg	$[HSO_4^-]$	$[H^+]$	$[Zr^{4+}] \cdot 10^9$	$[HR] \cdot 10^4$	
5	35	0.25	2.5	8024	0.390	0.220	0.280	3.14	4.70	4.01
10	70	0.50	2.0	11456	0.696	0.462	0.538	4.52	8.64	3.33
5	38	0.25	5.0	5062	0.123	0.220	0.280	1.03	7.10	2.35
5	38	0.50	2.0	7835	0.476	0.462	0.538	3.08	9.30	3.64
10	76	0.50	2.0	4940	0.300	0.462	0.538	1.95	12.90	1.55
5	39	0.27	5.0	3457	0.084	0.243	0.297	0.61	7.15	4.88
5	39	0.54	2.0	6419	0.390	0.510	0.570	2.29	9.84	4.92
5	44	0.25	25.0	1220	0.0059	0.220	0.280	0.05	12.80	4.58
5	44	0.50	10.0	7819	0.095	0.462	0.538	0.61	13.7	3.90
5	44	1.00	1.0	9053	1.10	0.945	1.055	14.7	22.5	0.41

In accordance with formula (2), the zirconium concentration should change in proportion to the fourth power of the hydrogen-ion concentration (for a constant concentration of the precipitant) and should be inversely proportional to the fourth power of the precipitant concentration (for a constant hydrogen-ion concentration).

From the results given in the table (taking into account the corrections for hydrolysis and formation of sulfate complexes) it is clear that the values obtained correspond to the given law.

From the results given in the table, it is clear that in most experiments, the values for $K_{eq.}$ differ from the mean value by not more than 1.5-2 times. Taking into account that the value of $K_{eq.}$ is very large ($3.36 \cdot 10^{19}$), such a deviation cannot give an error during the calculation of the solubility product

$$L_s = \frac{K_S^4}{K_{eq}} = \frac{(5,3 \cdot 10^{-5})^4}{3,36 \cdot 10^{19}} = 2,35 \cdot 10^{-37}.$$

A simple comparison of the solubility product of the cupferronates of zirconium ($2.35 \cdot 10^{-37}$) and aluminum ($2.3 \cdot 10^{-19}$) shows that it should be easy to find the optimum conditions for quantitative separation of these two elements.

The solubility of zirconium cupferronate in water can then be calculated from the value found for the solubility product. In view of the very low solubility of zirconium cupferronate, its saturated solutions are extremely dilute, and it is possible to assume that the activity coefficient is equal to one; then, for $L_s = [Zr^{4+}][R^-]^4$ the solubility

$$S_{Zr} = \sqrt[5]{\frac{L_s}{256}} = \sqrt[5]{\frac{2,35 \cdot 10^{-37}}{256}} = 1,6 \cdot 10^{-8} \text{ mole/liter.}$$

When the work described here was finished, the results of the work carried out by Elving and Olson was published [9]. These authors studied the solubility of the inner-complex compounds of the metals of the fourth group with aromatic nitrosohydroxylamines. Their method consisted in determining the nitrosophenylhydroxylamine concentration of the filtrate polarographically (in a nitrogen stream), after equilibrium has been established between the cupferronate and the solution of the acid. According to their results, the solubility of zirconium cupferronate is $2.3 \cdot 10^{-8}$ mole/liter. The agreement with our result ($1.6 \cdot 10^{-8}$ mole/liter) is quite satisfactory.

Using the equilibrium constants, it should be possible to carry out approximate calculations of the solubility of zirconium cupferronate, under the conditions used for precipitation, as a function of the concentration of acid and excess precipitant in solution.

SUMMARY

The equilibrium constant of the precipitation of zirconium with cupferron has been determined; it was found to be $3.36 \cdot 10^{19}$. The solubility product ($2.35 \cdot 10^{-37}$) and the solubility of zirconium cupferronate were calculated on the basis of the equilibrium constant. The value found for the solubility, $1.6 \cdot 10^{-8}$ mole/liter, agrees satisfactorily with published results.

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THE EFFECT OF CERTAIN IONS ON THE PRECIPITATION OF URANYL FERROCYANIDE FROM AQUEOUS SOLUTIONS

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In a previous paper [1] results were given of a study by the method of amperometric titration of the conditions for the precipitation of uranyl ions from aqueous solutions by potassium ferrocyanide, while the solubility of the precipitate formed $K_4(UO_2)_4[Fe(CN)_6]_3$ was also determined.

The most favorable medium for the amperometric titration of uranyl by ferrocyanide is a 1 M solution of potassium nitrate at a pH of 3.0-5.0, while the titration temperature should be 40-60°.

In view of the capacity of ferrocyanide to give precipitates with many multivalent cations, the composition of which depends on the anions and univalent cations present in solution, it was of interest to study the effect of a number of salts on the amperometric titration of uranyl by ferrocyanide.

Cations. a) Univalent Me^+. In order to evaluate the effect of ammonium and sodium ions on the results of amperometric titration, titration of uranyl nitrate was carried out in the presence of potassium nitrate on the one hand, and ammonium or sodium nitrate on the other. On replacing from 0 to 100% of the potassium nitrate with ammonium or sodium nitrate, the equivalence point, and, consequently, the molecular ratio $UO_2^{2+}/Fe(CN)_6^{4-}$ remained almost unchanged.

b) Divalent Me^{2+}. Of the divalent metals, zinc, copper, nickel, and lead ions form the least-soluble ferrocyanides. Since the solubility of uranyl ferrocyanide is also very low, it was of interest to establish the sequence in which the precipitates of these ferrocyanides are formed.

Zinc. In a 1 M potassium nitrate solution, zinc ions are clearly titrated by ferrocyanide with formation of a white precipitate of $K_2Zn_3[Fe(CN)_6]_2$. When uranyl ions are present during the titration, initially, a white precipitate of the zinc compound separates out; this subsequently acquires a brown color as a result of the uranyl ferrocyanide that is precipitated.

At the equivalence point, the amount of ferrocyanide used up is equal to the sum of the equivalents of zinc and uranyl, which are calculated from the molar ratios: $Zn^{2+}/Fe(CN)_6^{4-} = 1.5$; $UO_2^{2+}/Fe(CN)_6^{4-} = 1.33$.

The titration curves obtained thereby have the usual shape. All this indicates that when zinc and uranyl ions are present together, the titration proceeds quantitatively, without any change in the composition of these ferrocyanides.

Copper. Titration proceeds differently in the presence of copper ions. Copper ions give precipitates with ferrocyanide which are similar in color to that of the uranyl ferrocyanide precipitate, so that it is not possible to observe visually the sequence in which they are formed.

Both in the pure forms and in mixtures with uranyl ions, copper ions give clearly defined titration curves on titration with ferrocyanide.

As is evident from Table 1, during titration of a solution containing copper alone, ferrocyanides of variable composition are formed when the copper content is low.

For copper contents greater than 0.06 millimole, the precipitate acquires a constant composition, in which the ratio $Cu^{2+}/Fe(CN)_6^{4-} = 1.5$. The double ferrocyanide salt $K_2Cu_3[Fe(CN)_6]_2$ could correspond to this ratio.

The presence of uranyl ions does not affect the molecular ratio

$$\Sigma(Cu^{2+} + UO_2^{2+})/Fe(CN)_6^{4-} = 1,5,$$

as long as there is more than 5 millimole Cu^{2+} for one millimole UO_2^{2+}.

At lower copper contents the molar ratio $(UO_2^{2+} + Cu^{2+})/[Fe(CN)_6]^{4-}$ acquires a value approximating to 1.33, which is characteristic of the double salt of uranyl with potassium ferrocyanide:

$$K_4(UO_2)_4[Fe(CN)_6]_3.$$

The constancy of the molar ratios in the precipitates indicates that Cu^{2+} and UO_2^{2+} ions are capable of mutual isomorphous substitution, and consequently the composition of the ternary salt can be expressed in the first case by:

$$K_2(Cu, UO_2)_3[Fe(CN)_6]_2;$$

and in the second case by:

$$K_4(Cu, UO_2)_4[Fe(CN)_6]_3.$$

TABLE 1

Results of the Amperometric Titration of Solutions of Uranyl and Copper by Means of Ferrocyanide

Taken, millimole		Molar ratio Cu^{2+}/UO_2^{2+},	$K_4Fe(CN)_6$ used, mmole	Molar ratio $\Sigma(Cu^{2+}+UO_2^{2+})$ $Fe(CN)_6^{4-}$,	Composition of salt corresponding to given ratio
Cu^{2+}	UO_2^{2+}				
0	0,01	0 : 1	0,0078	1,29	$K_4(UO_2)_4\cdot[Fe(CN)_6]_3$
0,01	0,1	1 : 10	0,0840	1,27	$K_4(Cu, UO_2)_4\cdot$ $\cdot[Fe(CN)_6]_3$
0,01	0,05	1 : 5	0,0465	1,29	
0,01	0,02	1 : 2	0,0232	1,29	
0,01	0,01	1 : 2	0,0232	1,29	
0,01	0,01	1 : 1	0,0145	1,37	
0,01	0,01	1 : 1	0,0145	1,37	
0,01	0,01	2 : 1	0,0224	1,34	
0,03	0,01	3 : 1	0,0290	1,37	
0,05	0,01	5 : 1	0,0370	1,63	$K_2(Cu, UO_2)_3\cdot$ $\cdot[Fe(CN)_6]_2$
0,10	0,01	10 : 1	0,0750	1,47	
0,15	0,01	15 : 1	0,0960	1,55	
0,06	—	6 : 0	0,0415	1,45	$K_2Cu[Ee(CN)_6]_2$
0,10	—	10 : 0	0,0663	1,51	
0,20	—	20 : 0	0,1280	1,56	
0,30	—	30 : 0	0,1940	1,55	

Nickel. Nickel ions are readily titrated with ferrocyanide to form a white precipitate. The molar ratio $Ni^{2+}/Fe(CN)_6^{4-} = 1.29$ at the equivalence point in this case; this corresponds to the double salt $K_4 \cdot Ni_4[Fe(CN)_6]_3$.

When a mixture of Ni^{2+} and UO_2^{2+} ions is titrated, a brown-colored precipitate is formed. The ferrocyanide used up is equal to the sum of the amounts required for the titration of each ion separately. The ratio $\Sigma(Ni^{2+} + UO_2^{2+})/[Fe(CN)_6]^{4+}$ has a mean value of 1.33 ± 0.10, i.e., it has the same value as that obtained during the titration of pure uranyl.

The fact that the composition of the double salts of the ferrocyanides of nickel and uranyl is the same prevents one from solving the question of the sequence in which the double salts are formed, or whether a ternary salt $K_4(Ni, UO_2)_4[Fe(CN)_6]_3$ is formed at the same time.

Lead. The titration curves obtained during the titration of a solution of a pure lead salt are not so clearly defined.

At low concentrations (0.01 millimole in 10 ml) of lead, during titration there is observed the phenomenon of supersaturation, so that the white precipitate of lead ferrocyanide is only formed on addition of a certain excess of $K_4Fe(CN)_6$. The appearance of a precipitate is accompanied by a sharp drop in the diffusion current.

To an accuracy of up to 10%, the molar ratio $Pb^{2+}/[Fe(CN)_6]^{4-} = 2.1 \pm 0.20$, which corresponds to the formula for a simple salt $Pb_2 \cdot Fe(CN)_6$. During titration of a mixture of Pb^{2+} and UO_2^{2+} ions there is formed a brownish precipitate, in which the mean molar ratio $\Sigma(Pb^{2+} + UO_2^{2+})/[Fe(CN)_6]^{4-} = 2.0 \pm 0.10$. The apparently incomprehensible effect shown by lead can be clarified if one assumes that the lead ions replace the potassium ions in the double salt, with formation of the compound: $Pb_2(UO_2)_4[Fe(CN)_6]_3$, while the excess lead ions form a simple ferrocyanide.

Such an assumption would appear to be possible if one bears in mind the similarity of the ionic radii of lead and potassium.

Attempts to eliminate interference on the part of the divalent metals listed, by masking them with sodium ethylenediaminetetracetate (EDTA-Na), did not give positive results.

Addition of EDTA-Na in amounts which were twice and three times that necessary with respect to the equivalent amount of these metals, led to their complete masking as a result of the formation of compounds which are more stable than ferrocyanides.

However, EDTA-Na when present in excess amounts completely complexes UO_2^{2+} so that amperometric titration of the latter becomes impossible.

TABLE 2

Amperometric Titration of Uranium in the Presence of Aluminum, Chromium, and Cerium

Taken, mmole				Molar ratio Me^{3+}/UO_2^{2+}	$K_4Fe(CN)_6$ used, ml	Note
Al^{3+}	Cr +	Ce^{3+}	UO_2^{2+}			
—	—	—	0,01	0 : 1	0,80	
0,10				1 : 0	Not titrated	
0,50				5 : 0	»	
0,01			0,01	1 : 1	0,90	Titration curves clearly defined
0,05	—	—	0,01	5 : 1	0,90	
0,10	—	—	0,01	10 : 1	0,88	
0,30	—	—	0,01	30 : 1	0,90	
0,50	—	—	0,01	50 : 1	0,90	
0,80			0,01	80 : 1	1,00	Titration curves not clearly defined
1,00	—	—	0,01	100 : 1	1,00	
—	0,01	—	—	1 : 1	Not titrated	
—	0,05			5 : 1	»	
—	0,01	—	0,01	1 : 1	0,85	Titration curve not completely clearly defined
—	0,02	—	0,01	2 : 1	0,80	
—	0,03		0,01	3 : 1	0,80	
—	0,05		0,01	5 : 1	0,80	
—	—	0,005	—	0 : 0,5	Not titrated	
—	—	0,010	—	0 : 1	»	
—	—	0,0025	0,01	0,25 : 1	0,85	Titration curves clearly defined
—	—	0,0050	0,01	0,5 : 1	0,85	
—	—	0,010	0,01	1 : 1	0,85	
—	—	0,025	0,01	2,5 : 1	0,90	
—	—	0,050	0,01	5,0 : 1	0,95	

c) Trivalent Me^{3+}. Aluminum, chromium (III), cerium (III). Aluminum (III), chromium (III), and cerium (III) ions are not titrated in 1 M KNO_3 solution at a pH of 4.0-5.0 by ferrocyanide. Solutions containing the ions listed in amounts up to 0.1 millimole in 10 ml and a small excess of ferrocyanide do not give precipitates. When these ions are present together with uranyl ions in solution, precipitates of uranyl ferrocyanide of the normal type are formed.

The composition of the ferrocyanide precipitate does not change. This follows, as is evident from Table 2, from the fact that the amount of ferrocyanide used up at the equivalence point remains almost the same whether uranium alone is titrated or whether it is titrated together with the elements listed. The influence of these ions is only manifested in the rate at which the precipitate of uranyl ferrocyanide is formed; this leads to distortion of the lower part of the titration curves and renders establishment of the equivalence point difficult.

As indicated in Table 2, the titration curves still have a normal shape as long as the content of the elements listed does not exceed the uranium content by more than 50 times in the case of aluminum, 3-4 times in the case of chromium, and by more than 5 times in the case of cerium.

Iron. Iron (III) ions form a precipitate of Prussian blue with ferrocyanide in a potassium nitrate solution. The solubility of this compound is less than that of uranyl ferrocyanide. This follows from the fact that during titration of a mixture of these ions, initially, a blue precipitate of iron is formed; subsequently, as the brown precipitate of uranyl ferrocyanide is formed, the iron ferrocyanide acquires a greenish shade.

Iron (III) present in any amounts increases the results of the amperometric titration of uranyl.

It might be expected that iron (II) ions will not interfere with the titration of uranium in view of the comparatively high solubility of iron (II) ferrocyanide.

However, in a pure solution of 1 M potassium nitrate at a pH of 3.5-5.0, it is difficult to establish conditions under which iron (II) ions are not oxidized to the trivalent state.

Iron can only be kept in the divalent state in the presence of a reducing agent or complexing agents.

Ascorbic acid and hydroxylamine hydrochloride were tested as reducing agents. We were unable to use them, since ascorbic acid complexes uranyl fairly strongly and depresses the titration results, while hydroxylamine hydrochloride did not reduce the ferric ions completely.

Negative results were also obtained when EDTA-Na and potassium fluoride were tried.

d) Quadrivalent Me^{4+}. Thorium (IV). In a supporting electrolyte of potassium nitrate, thorium is clearly titrated with ferrocyanide to form a white precipitate which does not separate out readily.

TABLE 3.

Amperometric Titration of Thorium with Potassium Ferrocyanide

Taken, mmole		$K_4Fe(CN)_6$ used, mmole	$Th^{4+}/Fe(CN)_6^{4-}$	$\Sigma(Th+UO_2^{2+})/Fe(CN)_6^{4-}$
Th^{4+}	UO_2^{2+}			
0,00395	—	0,00436	0,905	—
0,00395	—	0,00340	1,165	—
0,00395	—	0,00436	0,900	—
0,00790	—	0,00680	1,160	—
0,00790	—	0,00680	1,160	—
0,00790	—	0,00680	1,160	—
0,00790	—	0,00820	0,960	—
0,0158	—	0,0145	1,090	—
0,0158	—	0,0145	1,090	—
0,0236	—	0,0208	1,170	—
0,0236	—	0,0232	1,010	—
		Mean	1,060	
—	0,010	0,0068		1,33
0,00395	0,010	0,0097		1,45
0,00790	0,005	0,0097		1,32

It follows from Table 3 that the ferrocyanide has the composition ThFe(CN)$_6$.

During titration of a mixture of uranyl and thorium ions, the first and subsequent drops of ferrocyanide lead to the appearance of a brown precipitate.

The volume of ferrocyanide solution is equal to the sum of the volumes of ferrocyanide required for the titration of each element taken separately.

No additional breaks are observed on the titration curves.

These observations indicate that the ferrocyanides of uranyl and thorium have roughly the same solubility, and that they are precipitated simultaneously during titration.

Anions. The effect of the following anions was studied: chloride, sulfate, phosphate, vanadate, molybdate, and chromate.

Chlorides. On replacing from 0 to 50% of the NO_3^- ions in a 1 M solution of potassium nitrate by an equivalent amount of chloride ions, it was established that the presence of chloride ions does not affect amperometric titration of uranium with ferrocyanide.

Sulfates. Satisfactory results are obtained on carrying out amperometric titration at room temperature, even when the potassium nitrate is completely replaced by potassium sulfate. Compared with a pure solution of potassium nitrate, titration proceeds considerably more slowly. Sulfate ions show a marked effect on increasing the temperature. It has been established previously [1] that, in the presence of sulfates, the solubility of the uranyl ferrocyanide precipitate increases sharply with increasing temperature. Thus, ferrocyanide which has been precipitated in the cold will dissolve completely on increasing the temperature to 80-90°, and will settle out again on cooling. This is of decisive importance for the amperometric titration of uranium carried out at 40-60°, even in those cases where the sulfate-ion content does not exceed 10% of the amount of potassium nitrate in solution.

It was noticed that at elevated temperatures, when sulfate ions are present in solution, the platinum electrode is readily passivized and loses its sensitivity. Under such conditions the platinum surface becomes covered with a blue film. The sensitivity of the electrode can be restored by treating the surface with alkali and nitric acid.

Phosphates. Uranyl ions are quantitatively precipitated by phosphate ions from a 1 M potassium nitrate solution at pH 3.0-5.0. Under the conditions used for amperometric titration, the solubility of the phosphate is less than the solubility of the uranyl ferrocyanide, as a consequence of which, the experimental results obtained for uranium are strongly depressed. Attempts to mask phosphate ions by means of magnesium ions, which themselves do not interfere with the titration, did not give positive results.

TABLE 4. Amperometric Determination of Uranium in the Presence of Vanadate

VO_3 taken, mmole	UO_2^{2+} taken, mmole	Ratio VO_2^-/UO_2^{2+}, mmole	$K_4Fe(CN)_6$ used, ml	VO_3 taken, mmole	UO_2^{2+} taken, mmole	Ratio VO_2^-/UO_2^{2+}, mmole	$K_4Fe(CN)_6$ used, ml
–	0.010	0:1	0.80	0.03	0.010	8:1	0.75
0.02	–	2:0	Not titrated	0.08	0.010	8:1	0.80
0.08	–	8:0	" "	0.16	0.010	16:1	0.85
0.20	–	20:0	" "	0.40	0.015	27:1	1.27
0.80	–	80:0	" "	0.40	0.15	27:1	1.25
0.04	0.010	4:1	0.80	0.40	0.010	40:1	0.85
0.04	0.010	4:1	0.80	0.40	0.010	40:1	0.90

Vanadates. Vanadate ions present in a 1 M potassium nitrate solution at pH 4.0-5.0 do not interfere with amperometric determination.

As is evident from Table 4, satisfactory titration results can be obtained even when the amount of vanadate present is 30-40 times that of the uranium present.

Tests showed that it is necessary to control the acidity of the medium rigidly (pH 4.0-5.0) in order to obtain reliable results. At higher pH, precipitation of uranyl is delayed, while at lower pH, the results obtained are high because of the interaction of ferrocyanide and vanadate.

When the pH is sufficiently low, oxidation of ferrocyanide by the vanadate can occur.

The quadrivalent vanadium ions which are formed as a result of this reaction are precipitated by excess ferrocyanide in the form of a yellow precipitate which changes (on standing) subsequently to green.

When the interaction between ferrocyanide and vanadate is carried out in the presence of any reducing agent, e.g., ascorbic acid, formation of the yellow precipitate starts at pH higher than 5.

Thus, if uranium is to be titrated amperometrically in the presence of vanadium, reducing agents must be absent.

The requisite pH can be established by using a mixed indicator, for this purpose an equal number of drops of 0.1% solutions of methyl orange (aqueous solution) and bromophenol blue (alcoholic solution) are added to the test solution.

The final color of the test solution is compared with the color of a buffer solution with a pH of 4.5.

Molybdate. In the pH range 3.0 to 5.0, molybdate does not react with ferrocyanide, but reacts with uranyl ions, precipitating them in the form of uranyl molybdate. Low results are obtained during amperometric titration of uranium in the presence of molybdate ions.

Chromate. At pH 3-5, chromate ions do not oxidize ferrocyanide and do not interfere with amperometric titration.

At lower pH values, oxidation of ferrocyanide occurs. At pH about 1.0, chromate can be quantitatively titrated with ferrocyanide.

This study of the effect of certain ions on the amperometric titration of uranium with ferrocyanide allows one to divide all the elements tested into the two following groups:

Ions which interfere with uranium determination	Ions which do not interfere with uranium determination
Zinc	Ammonium
Copper	Sodium
Nickel	Magnesium
Lead	Aluminum
Iron (III)	Chromium (III)
Thorium	Cerium (III)
Phosphates	Chlorides
Molybdates	Vanadates
Sulfates (partially)	Chromates

The experiments which we have carried out confirm once again the general opinion regarding the complexity of the chemistry of the ferrocyanides.

The amperometric-titration method has shown itself to be a convenient means for studying the reaction products obtained during the interaction of ferrocyanide with various ions.

A study of the interaction of ferrocyanides with the oxy ions of vanadium, molybdenum, chromium, etc., should obviously be of special interest. Thanks to the work, mainly of I.V. Tananaev et al. and O.A. Songina, the question of the interaction of ferrocyanide with divalent metal ions has been dealt with in the literature. On the other hand, the interactions of ferrocyanide with the oxy ions has hardly been touched upon in the literature, although the study of such interactions could lead to the development of new methods for determining them.

The results which we have obtained by means of amperometric titration on the composition of the precipitates of the binary salts of potassium ferrocyanide with divalent metal ions agree with the results obtained by other methods.

Thus, the precipitate of zinc ferrocyanide corresponds in its composition to the generally accepted formula: $K_2Zn_3[Fe(CN)_6]_2$.

The composition of the precipitate of lead ferrocyanide $Pb_2[Fe(CN)_6]$ agrees with the results of Treadwell [2] and Songina [3].

The composition of the nickel salt $K_4Ni_4[Fe(CN)_6]$ agrees with the results of Tananaev and Levina [4].

The composition of the double copper salt $K_2Cu_3[Fe(CN)_6]_2$ does not confirm the results of Chovnyk and Kleibs [5] and Chovnyk and Kuz'mina [6], but agrees with the results of Tananaev and Glushkova [7], who found a similar compound for the double salt of copper and thallium.

Our results on the composition of thorium ferrocyanide $ThFe(CN)_6$ agree with those of Glushkova [8], while our results on the mixed ferrocyanide of uranyl and potassium $K_4(UO_2)_4[Fe(CN)_6]_3$ agree with those of Tananaev and Levina [9].

Of special importance is the participation of uranyl ferrocyanide in the formation of ternary salts with copper, nickel, and lead. Copper ferrocyanide belongs to the class of very sparingly soluble compounds. Accordingly, isomorphous substitution of part of the copper by uranyl may prove to be a means for the quantitative separation of uranium. This could be all the more useful since uranium can be readily separated from copper and ferrocyanide by treating the precipitate obtained with ammonia.

The very clearly defined curves obtained during the amperometric titration of thorium with ferrocyanide could be used as a basis for the quantitative determination of thorium, especially, as we have shown, since cerium (III) salts are not titrated under these conditions.

SUMMARY

The effect of certain cations and anions on the composition of the precipitate formed by the interaction of uranyl and ferrocyanide ions has been studied by amperometric titration.

It has been shown that NH_4^+, Na^+, Mg^{2+}, Al^{3+}, Cr^{3+}, Ce^{3+}, VO_3^-, CrO_4^-, and Cl^- do not alter the composition of uranyl ferrocyanide $K_4(UO_2)_4[Fe(CN)_6]_3$ and do not interfere with the titration, while Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Th^{4+}, MoO_4^{2-}, PO_4^{3-}, SO_4^{2-} interfere with the titration, forming, in some cases, more complicated compounds.

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DETERMINATION OF URANIUM BY AMPEROMETRIC TITRATION

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Uranium has been titrated amperometrically by a number of authors [1-5]. Kolthoff and Johnson [1] titrated uranium with nitrophenylarsonic acid using the diffusion current of uranium and nitrophenylarsonic acid (the wave obtained by the reduction of the nitro group to the amino group). Kolthoff and Kohn [2] have developed a technique for titrating phosphates with a uranium solution using the diffusion current of uranium. Uranium is reduced on a dropping mercury electrode; accordingly, uranium can be titrated amperometrically on a dropping-mercury electrode by many precipitants. Such a method, however, is not sensitive enough.

Amperometric methods which are based on oxidation-reduction reactions are more sensitive. In these cases, titration is usually carried out on a platinum indicator electrode, which permits one to work with such strong oxidizing agents as ammonium vanadate, potassium dichromate, etc.

Amperometric titration of uranium using a platinum electrode is carried out on the basis of the diffusion current of the titrant.

In the work described here, a study was made of the conditions required for the direct amperometric titration of uranium by means of ammonium vanadate using a platinum microelectrode.

EXPERIMENTAL

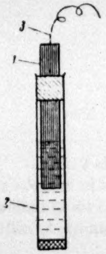

Fig. 1. Bismuth reference electrode: 1) rod of bismuth metal; 2) test tube with porous bottom filled with 12 N H_2SO_4; 3) contact for connecting the electrode to the external circuit.

Titration was carried out on a "Gintsvetmet" polarograph with a mirror galvanometer having a sensitivity of $2.4 \cdot 10^9$ amp/mm/m. The indicator electrode was a platinum wire 15 mm long and 0.5 mm in diameter fused into the end of a glass tube. The electrode was rotated at the rate of 750 rpm by means of a synchronous motor. The platinum wire was dipped now and again in a chromic mixture and washed with distilled water.

A bismuth electrode (Fig. 1) was used as the reference electrode.

According to Syrokomskii's results [6], the oxidation-reduction potential of the system V^V/V^{IV} increases with increasing acidity. In 12 N H_2SO_4, it is equal to +1.22 volts. Under these conditions, the reaction between quadrivalent uranium and ammonium vanadate proceeds rapidly.

The anode-cathode curves obtained (Fig. 2) on the platinum electrode indicate that ammonium vanadate in 12 N sulfuric acid gives a clearly defined diffusion current in the range +0.2 to −0.2 volts with respect to the saturated calomel electrode (or from +0.18 to −0.22 volts with respect to the bismuth electrode).

The maximum diffusion current occurs at 0-0.2 volts as is evident from Fig. 2; accordingly, titration can be carried out without applying an external potential, and this appreciably simplifies the apparatus.

A study of the effect of the acidity of the medium on the nature of the anode-cathode curves for ammonium vanadate showed that, within the limits 8 to 16 N, there is no change in the nature of the curves.

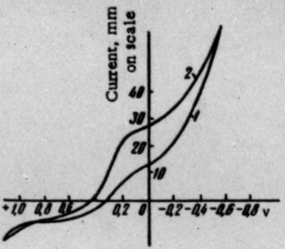

Fig. 2. Anode-cathode curves for ammonium vanadate in 12 N H_2SO_4: 1) 0.001 N NH_4VO_3; 2) 0.01 N NH_4VO_3.

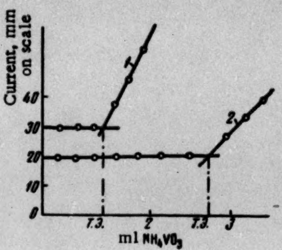

Fig. 3. Curves obtained during titration of 0.200 mg uranium with ammonium vanadate: 1) 0.001 N NH_4VO_3; 2) 0.000* N NH_4VO_3; galvanometer sensitivity 1/10.

TABLE 1

Comparative Titration of Quadrivalent Uranium After Phosphate Precipitation

Vanadate concentration	Uranium introduced, mg	NH_4VO_3 used, ml		Uranium found, mg		Absolute error, mg		Relative error, %	
		Amperometrically	Using indicator	Amperometrically	Using indicator	Amperometrically	Using indicator	Amperometrically	Using indicator
0,001	0.2	1,50	2,00	0,179	0,238	−0,021	+0,038	−10,5	+19
		1,50	2,10	0,179	0,250	−0,021	+0,050	−10,5	+25
		1,50	2,05	0,179	0,244	−0,021	+0,044	−10,5	+22
		1,50	2,10	0,179	0,250	−0,021	+0,050	−10,5	+25
		1,50	2,00	0,179	0,238	−0,021	+0,038	−10,5	+15
				Mean		−0,021	+0,044	−10,5	+22
0,001	0,1	0,78	1,05	0,093	0,125	−0,007	+0,025	−7	+25
		0,76	1,05	0,091	0,125	−0,009	+0,025	−9	+25
		0,76	1,05	0,091	0,125	−0,009	+0,025	−9	+25
		0,77	1,05	0,092	0,125	−0,008	+0,025	−8	+25
		0,78	—	0,093	0,125	−0,007	—	−7	+25
				Mean		−0,008	+0,025	−8	+25
0,0002	0,025	1,00	—	0,0239	—	−0,0011	—	−4,4	—
		1,10	—	0,0262	—	+0,0037	—	+14,8	—
		1,15	—	0,0273	—	+0,0048	—	+19,2	—
				0,0239	—	−0,0011	—	−4,4	—
				Mean		+0,0005	—	+4,0	—
0,0002	0,0125	0,54	—	0,0128	—	+0,0003	—	0,0	—
		0,53	—	0,0126	—	+0,0001	—	+0,8	—
		0,56	—	0,0133	—	+0,0008	—	+6,4	—
				0,0133	—	+0,008	—	+6,4	—
				Mean		+0,0005	—	+4,0	—
0,0002	0,0062	0,26	—	0,0062	—	0,0000	—	+0,0	—
		0,28	—	0,0067	—	+0,0005	—	+8,0	—
		0,27	—	0,0065	—	+0,0003	—	+4,8	—
		0,27	—	0,0065	—	+0,0003	—	+4,8	—
		0,26	—	0,0062	—	+0,0000	—	+0,0	—
				Mean		+0,0002	—	+3,5	—

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*As in the original — Publisher's note.

The largest potential jump during the potentiometric titration of uranium with ammonium vanadate, and the sharpest break on the amperometric curve are obtained in 8-16 N sulfuric acid.

In Fig. 3 are shown the curves obtained during titration of 0.200 mg of uranium with ammonium vanadate solution in 12 N sulfuric acid.

In order to evaluate the sensitivity of the method, uranium was reduced in a bismuth reducer or by means of electrolysis on a mercury cathode, and then titrated with ammonium vanadate in 12 N sulfuric acid. The total volume of solution was 25 ml. As a result of these experiments, it was established that even on titrating such small amounts as 25 $\gamma - 1$ mg of uranium the relative error was only 2-3%.

The method was checked on production samples. The samples were prepared by the hydrosulfite-phosphate or by the chromo-phosphate methods [7].

Table 1 contains the results obtained on titrating pure solutions of uranium with ammonium vanadate after preparing the samples by the hydrosulfite-phosphate method. They show that amperometric titration is definitely superior to an indicator method; when an indicator is used, the results are much too high, the results being higher the less the amount of uranium being titrated.

TABLE 2

Determination of the Uranium Content of Coal Cakes by Amperometric Titration

Uranium cont. of aliquot of sample,* mg	Uranium intro-duced, mg	Tot. uranium cont., mg	Uranium found, mg	Error	
				Abs., mg	Rel., %
0,118	0,05	0,168	0,169	+0,001	+0,6
0,042	0,05	0,092	0,095	−0,003	+3,26
0,495	0,05	0,545	0,535	−0,010	−1,84
0,034	0,05	0,084	0,082	−0,002	−2,38
0,035	0,05	0,085	0,082	−0,003	−3,52
0,057	0,05	0,107	0,111	+0,004	+3,61
0,033	0,05	0,083	0,085	+0,002	+2,35
0,045	0,05	0,095	0,095	−0,000	0,00
0,043	0,05	0,093	0,093	0,000	0,00
5,80	0,05	5,85	6,25	+0,400	+6,83

*Determined amperometrically.

Table 2 contains results obtained by amperometric determination of uranium in coal cakes, with and without addition of uranium prior to decomposition of the samples: to an aliquot of cake (0.5 g) was added 0.5 mg uranium (1 ml of a solution containing 0.5 mg uranium/ml); the sample was then processed further by the hydrosulfite-phosphate or the chromo-phosphate methods.

Amperometric titration was applied to the determination of uranium in wastes from technological processing and in production solutions. The results were compared with those obtained on titrating with an indicator (phenylanthranilic acid and barium diphenylaminosulfonate).

TABLE 3

Amperometric Determination of Uranium in Standard Ores

Specified uranium content, %	Uranium found, %*
0,072±0,003	0,070±0,0003
0,237±0,003	0,236±0,002
0,103±0,002	0,098±0,001
0,059±0,004	0,059±0,001
0,081±0,004	0,084±0,003

*All the samples were air dry.

Application of amperometric titration to the analysis of production samples showed that the use of amperometric titration instead of titration by means of an indicator in the hydrosulfite-phosphate and chromo-phosphate methods leads to a considerable increase in both the sensitivity and accuracy of the method.

The method was checked on standard samples of uranium ores (Table 3).

Analytical procedure. The amount of sample taken depends on the uranium content: for 1-0.01% U the sample taken should be 0.2-0.5 g, and the strength of the ammonium vanadate solution 0.01 N; for 0.1-0.01% U, the sample should be 0.5-1 g and the strength of the ammonium vanadate 0.01 N; for 0.01-0.0005% U, the sample should be 1 g and the strength of the ammonium vanadate 0.0002 N. The sample is given a preliminary chemical treatment by the hydrosulfite-phosphate or the chromo-phosphate methods [7]. After decomposition of the ores and removal of the insoluble part, the acid solution is neutralized with ammonia using methyl yellow (pH 2.3) as indicator, 3 ml of concentrated hydrochloric acid is then added and the solution diluted to 200 ml. To this solution is added 10 ml of a 10% solution of disodium hydrogen phosphate, sodium hydrosulfite (1 g per g of sample), 3-4 ml of thorium chloride (5 mg of thorium per ml), and a small amount of paper pulp. After coagulation, the precipitated phosphates of uranium and coprecipitant are filtered under vacuum through a No. 3 filter funnel with porous glass or through a Buchner funnel ("blue or white band"). The uranium phosphate is dissolved on the filter in 8-16 N sulfuric acid; three to four lots of 10-15 ml of the latter are used, each aliquot being sucked through into a clean flask after 5-10 minutes. The total volume of solution should not exceed 100 ml.

The solution is quantitatively transferred into a 150-200-ml beaker. In the chromo-phosphate variant of the method, after addition of phosphate, 0.5-15 g of solid ammonium thiocyanate is added (on the basis of 2.5 g of ammonium thiocyanate to 0.1 g of iron); this is followed by 0.5 N $CrCl_3$ solution until the red color of ferric thiocyanate disappears; 3 ml of the $CrCl_3$ solution is added in excess. The procedure subsequently followed is the same as that in the hydrosulfite-phosphate method.

Before titrating the test solution the requisite sensitivity of the galvanometer is chosen. This is established by lowering the electrodes into a solution of 12 N sulfuric acid, switching on the motor and galvanometer, and regulating, by means of a corrector, the position of the light spot of the galvanometer so that is is near to the zero of the scale. Then, while adding ammonium vanadate, the requisite sensitivity of the galvanometer is selected by means of a shunt (on adding 0.2 ml of ammonium vanadate the light spot should be displaced 2-4 cm along the scale). Having washed the electrodes with distilled water, they are lowered into the beaker containing the test solution. Ammonium vanadate solution is added to the solution in lots of 0.1-0.2 ml from a microburet, and the position of the light spot on the scale recorded each time. The equivalence point is established graphically.

SUMMARY

It has been shown that uranium (down to 1 γ/ml) can be titrated amperometrically with ammonium vanadate solution with an accuracy of 2-3%. A bismuth electrode is used as a reference electrode. No external potential is applied during titration.

The samples are prepared for titration by the hydrosulfite-phosphate or the chromo-phosphate methods.

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SEPARATION OF URANIUM FROM ACCOMPANYING METALS BY MEANS OF ION-EXCHANGE CHROMATOGRAPHY

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Separation of uranium from the elements accompanying it by means of ion-exchange chromatography is based on the relationship between the sorbability of the ions and the sign and value of the charge [1]. The use of the difference in the value of the charge is less effective from a practical point of view: in this way, uranium is separated in the main from some elements $U^{VI}-Th$; $U^{VI}-Fe^{III}$ [1-3].

In order to separate uranium, use is made of strongly basic anion exchange resins containing quaternary ammonium groups which selectively absorb the chloride [4-6], sulfate [7-8], carbonate [9], and acetate [10] complexes of uranium.

In order to separate uranium from the accompanying elements which are most difficult to separate (V, Mo, Fe^{III}, Cu, and Pb), we thought it would be best to use the difference in the capacity of the elements to form complexes with sodium ethylenediaminetetraacetate (EDTA-Na) [11].

Separation of Uranium from Accompanying Metals in the Presence of EDTA-Na on a Sulfonate Cation Exchange Resin

The ion-exchange resin used was the cation exchange resin KU-2 with a particle size of 0.25 mm; it was prepared according to GOST 5629-52. For each test, 10 ml of the cation exchange resin in the swollen state was used. The column, which was 25 cm long, had a diameter of 1 cm.

In order to establish the conditions necessary for separating the elements, a study was made of their behavior on the KU-2 cation exchange resin in the hydrogen and sodium forms, in the presence of EDTA-Na* at various pH values. EDTA-Na was added to the test solution in equimolar amounts** with respect to the components present; the pH was adjusted by means of ammonia (free from carbonate) using a glass electrode. The solution was passed through the column at the rate of 0.8 cm/minute. The contents of the various elements in the filtrates were determined photocolorimetrically (uranium by the peroxide method, molybdenum by the thiocyanate method; vanadium by the peroxide method, copper by the diethyldithiocarbamate method [13]). Tungsten was determined radiometrically on the basis of a β-count (when the test solution was prepared the W^{185} isotope was introduced); lead was determined polarographically [14]. In those cases where EDTA-Na interfered with determination of the element, it was removed by oxidizing the mixture with concentrated sulfuric and nitric acids.

For comparison, experiments were also carried out on the sorption of vanadium, molybdenum, and tungsten, obtained under similar conditions, but in the absence of EDTA-Na.

The curves in Figs. 1, 2, 3, and 4 illustrate the relation between completeness of sorption of the elements and the acidity of the medium.

Uranyl ions only exist in acid solutions, since at pH > 4.2 diuranates separate out. In the presence of EDTA-Na, this phenomenon is observed at pH > 9.2. With increasing pH of the original solution, sorption of uranium on

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*The commercial product was purified by a technique described in [12].

**This procedure was adopted throughout the subsequent experiments.

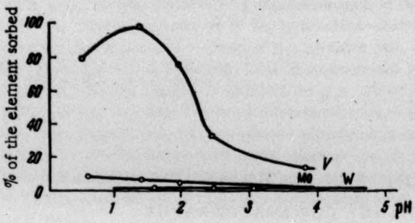

Fig. 1. Relation between the sorption of molybdenum, vanadium, and tungsten and the pH of the medium (cation exchange resin KU-2 in the hydrogen form).

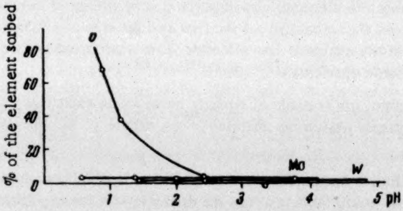

Fig. 2. Relation between the sorption of molybdenum, vanadium, and tungsten and the pH of the medium (cation exchange resin KU-2 in the sodium form).

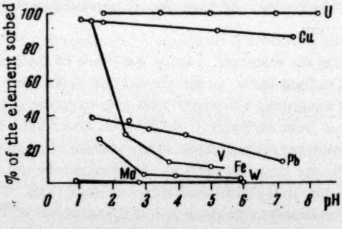

Fig. 3. Relation between pH of the medium and the sorption of uranium, molybdenum, vanadium, tungsten, iron (III), copper, and lead, in the presence of EDTA-Na (cation exchange resin KU-2 in the hydrogen form).

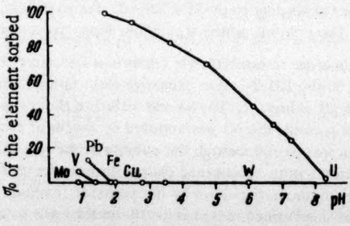

Fig. 4. Relation between the sorption of uranium, molybdenum, vanadium, tungsten, iron (III), copper, and lead, and the pH of the medium, in the presence of EDTA-Na (cation exchange resin KU-2 in the sodium form).

the cation exchange resin in the sodium form decreases, and in media approximating to neutral there is observed considerable (65-90%) breakthrough of the uranium through the column of cation exchange resin into the filtrate (Fig. 4). The latter can be explained by the formation of an anionic complex of uranium in solution.

We have shown earlier [15] that formation of a compound of uranium with EDTA-Na occurs at pH > 3; this does not contradict the results of other authors [16].

In the presence of EDTA-Na, quantitative sorption of uranium on the cation exchange resin in the hydrogen form, even from neutral solutions (Fig. 3), can only be explained by the breakdown of the complex compound of the acid which is formed as a result of the ion-exchange process. A comparison of the sorbability of Mo, W, and V in the absence (Figs. 1 and 2), and in the presence of EDTA-Na (Figs. 3 and 4), in acid media, showed that in the latter instance sorption is considerably lowered. For example, at pH 0.9 in the absence of EDTA-Na, 27.9% of the vanadium passes into the filtrate (Fig. 2), while in the presence of EDTA-Na, 94.4% passes into the filtrate (Fig. 4). The same phenomenon is observed in the case of molybdenum. Consequently, it can be assumed that, under the conditions indicated, compounds of these elements with EDTA-Na are formed.

Iron, copper, and lead form stable complex compounds of the anionic type with EDTA-Na; naturally, they are not sorbed on the cation exchange resin in the sodium form (Fig. 4).

Comparison of the curves obtained (Figs. 1-4) leads one to assume that, by using the cation exchange resin KU-2 in the sodium form, while the pH of the original solution is 1.7-1.9 and EDTA-Na is present, it should be possible to separate uranium from a large number of accompanying elements.* This assumption was checked on synthetic mixtures, in whose making up we were guided by the typical proportions of the elements in industrial samples.

EDTA-Na was added to synthetic mixtures containing various ratios of the components, and the procedure outlined above then followed. In preparing solutions containing uranium and tungsten, however, after addition of the EDTA-Na and neutralization, the mixture was heated** on a water bath for ten minutes, and after cooling was passed through the cation exchange resin. Molybdenum, vanadium, tungsten, and iron were determined in all the experiments in the combined filtrate and wash liquors.

Uranium was desorbed by means of a 10% solution of HNO_3 (passed through at the rate of 1.6 ml/minute), while the amount of it was determined by the peroxide method; alternatively, it was desorbed with 10% H_2SO_4 and determined vanadometrically [17].

The separation is completely satisfactory (Tables 1 and 2).

TABLE 1

U, mg		Error, %	Mo, mg		Error, %	V, mg		Error, %	W, mg		Error, %
taken	found		taken	found		taken	found		taken	found	
10,0	9,95	−0,5	10,0	10,0	0,0	—	—	—	—	—	—
12,40	12,43	+0,2	1,18	1,16	−1.6	—	—	—	—	—	—
12,40	12,45	+0,4	0,0987	0,099	+0,3	—	—	—	—	—	—
13,4	13,4	0,0	—	—	—	12,5	12,6	+0,8	—	—	—
13,4	13,5	+0,74	—	—	—	1,25	1,24	+0,8	—	—	—
13,4	13,5	+0,74	—	—	—	0,125	0,122	−2,4	—	—	—
15,4	15,25	−0,9	—	—	—	—	—	—	4,0	3,86	−3,5
12,56	12,56	+0	—	—	—	—	—	—	12,0	12,6	+5,0
40,0	39,8	−0,5	—	—	—	—	—	—	2,0	1,98	−1,0

Traces of copper, which were detected in the desorbed uranium solution for an original ratio of $C_U/C_{Cu} = 1$, were found to be very small, and do not essentially affect the results for uranium. Some complications develop only for $C_U/C_{Pb} = 1$; however, we did not come across such ratios in the samples that were analyzed.

The method was tested, first of all, on uranium-rich materials in which the elements accompanying uranium were present in small amounts, namely, in uranium-molybdenum, uranium-tungsten alloys, and in certain concentrates.

An aliquot of test material (0.5 g) was broken down with aqua regia (alloys) or with perchloric acid (concentrates). The solution obtained was transferred into a standard flask (250 ml), and an aliquot of this solution

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*The results of the separation of uranium from vanadium and molybdenum on the sulfonate cation exchange resin, as well as individual results given in Tables 1 and 4, were obtained by A.V. Yamshchikov.

**Heating accelerates dissolution of the uranyl tungstate, which is formed initially on pouring the original solutions of the components together, in the absence of EDTA-Na.

TABLE 2

U, mg		Error, %	Fe, mg		Error, %	Cu, mg		Pb, mg	
taken	found		taken	found		taken	found in desorbed uranium solution	taken	found in desorbed uranium solution
10,65	10,65	0,0	19,6	19,5	−0,5	—	—	—	—
22,05	22,0	−0,23	2,0	1,98	−1,0	—	—	—	—
1,0	0,985	−1,5	50,0	49,5	−1,0	—	—	—	—
10,05	10,0	−0,5	—	—	—	10,0	0,02	—	—
10,05	10,04	−0,1	—	—	—	0,2	0,0	—	—
10,05	10,25	+1,99	—	—	—	—	—	10,0	0,193
10,05	10,15	+0,9	—	—	—	—	—	4,0	0,046
10,05	10,09	−0,0	—	—	—	—	—	0,2	0,0

containing, on an average, 10-20 mg of uranium taken for analysis, a 5% EDTA-Na solution was added (1-2 ml), and the pH adjusted to 1.7-1.9 while the volume was adjusted to 25-30 ml; the latter was then passed through the cation exchange resin in the sodium form at the rate of 0.8 ml/minute. After washing the column with water (150 ml passed through at the rate of 3.2 ml/minute), the uranium was desorbed with 3 N sulfuric acid, which was passed through at a rate of 1.6 ml/minute. The sulfuric acid solution issuing from the chromatographic column was passed through a bismuth reducer. In this way, desorption and reduction of uranium were realized simultaneously. Uranium was determined by titration with potassium dichromate. The results obtained are given in Table 3; they agree quite satisfactorily with the specified contents.

TABLE 3

Sample	U content, %			Content of other elements, %
	chromatographic method	hydrophosphate method	specified content	
Alloy of U and Mo	91,49	—	91,19	Mo 8,73
	91,24	—	—	—
	91,34	—	—	—
Alloy of U and W	96,103	—	—	—
	96,103	—	96,09	W 3,83
	96,24	—	—	—
	96,24	—	—	—
Concentrate	82,66	82,68	82,58	Contains
	82,66	—	±0,11	Ca, Al, Mn
Uranoso uranic oxide	82,22	—	—	—
	82,04	82,48	—	—
	82,57	—	—	—

The method described for separating uranium from accompanying elements was also tested out on ore materials.

In analyzing uranium ores, the difficulty arises of calculating the amount of EDTA-Na that should be added to mask the other elements. At pH 1.7-1.9 ethylenediaminetetraacetic acid (EDTA) has an insignificant solubility[*]; accordingly, excess of the uncombined EDTA passes into the precipitate and traps some of the uranium; this was shown spectrographically. Results of uranium determinations were low; for example, for sample 1[**] (see Table 4), we found 3.07-3.09% of uranium, whereas the true value was 3.33 ± 0.05%. Consequently, the amount of EDTA-Na added to the solution should be such as to prevent precipitation of EDTA.

Depending on the expected uranium content, 0.5-2.0 g of ore was decomposed with hydrochloric acid to

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[*] The solubility of ethylenediaminetetraacetic acid in 0.1 N HCl is 0.16 g/liter, in 0.01 N HCl it is 0.06 g/liter; the determinations were carried out by N.I. Udal'tsova.

[**] The amount of EDTA-Na added was one-and-a-half times the amount of sample taken.

TABLE 4

Ore No.	U content, %		Ore No.	U content, %	
	chromatographic method	specified content		chromatographic method	specified content
1	3,30	—	2	4,37	4,36±0,02
	3,35	—		4,365	—
	3,26	3,33±0,05		4,25	—
	3,28	—	3	0,120	—
	3,38	—		0,123	0,123±0,002
	3,32	—		0,126	—

which hydrogen peroxide had been added, or with aqua regia and hydrofluoric acid. Excess fluoride ions were removed by a double evaporation with concentrated nitric acid. The hydrochloric or nitric solutions obtained (volume 50 ml) were neutralized with dilute ammonia solution (free from carbonate) until the pH was 1.7-1.9; dry EDTA-Na was added gradually in small portions, and the procedure outlined above for the analysis of uranium-rich products then followed.

Despite the fact that the results obtained (Table 4) are satisfactory, determination of uranium by the given technique has considerable disadvantages; accordingly, the method described cannot be recommended for industrial laboratories.

Separation of Uranium from Accompanying Metals in the Presence of EDTA-Na on a Carboxyl Cation Exchange Resin

a) Ores containing n-0.n% uranium. The compound of uranium with EDTA-Na possesses low stability [15]. The chemisorption character of the absorption of uranium by carboxyl resins suggests the possibility that uranium will be sorbed by these ion exchange resins with destruction of the strongly dissociated complex.

The sorbent used was the carboxyl cation exchange resin Amberlite IRC-50 (10 ml) with a particle size of 0.25 mm.

It was found that at pH 2-8 in the presence of EDTA-Na this cation exchange resin quantitatively sorbed uranium. The pH range 5.5-7.0 was chosen for the separation. As tests showed, V, Mo, W, Fe (III) are not completely sorbed by cation exchange resins under the given conditions.

Ni, Co, Zn, Al, etc., in this pH range, form stable anionic complexes with EDTA-Na [11] and cannot be sorbed by the cation exchange resin.

First of all, the possibility of separating uranium from accompanying elements in the presence of EDTA-Na on a carboxyl cation exchange resin was checked on uranium ores containing whole percentages and tenths of a percent of uranium.

TABLE 5

Ore No.	U content, %		Ore No.	U content, %	
	chromatographic method	specified content		chromatographic method	specified content
3	0,125 0,122	0,123+0,001	1	3,28 3,29 3,36	3,30±0,06
4	0,613 0,615 0,615	0,609+0,004	5	0,212 0,210 0,208	0,22±0,01
2	4,33 4,36	4,36 ±0,02			

An aliquot of ore (1-4 g) was decomposed as described above. Into the solution thus obtained (50-75 ml) was added dry EDTA-Na (four times the amount of the aliquot). The pH of the solution was adjusted to 5.5-7.0, and it was then passed through a column of Amberlite IRC-50 in the sodium form at the rate of 0.8 cm/minute. The subsequent procedure adopted was similar to that used in the case of the sulfonate resin. The results are given in Table 5; the deviation from the specified contents is insignificant.

Other marks of carboxyl resins can be used in the variant just described for the chromatographic separation of uranium from accompanying elements.

b) Ores containing tenths and hundredths of a percent of uranium, and poor solutions from uranium production. Titration with potassium dichromate is not convenient in the case of small amounts of uranium; sorption of uranium is impossible from poor solutions from uranium production, usually soda solutions.

In this connection, we carried out a number of tests, the aim of which was to improve the method suggested earlier, as applied to poor uranium materials.

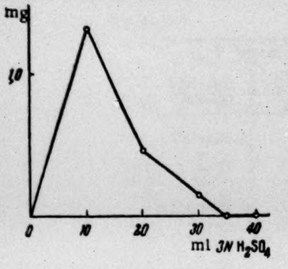

Fig. 5. Desorption curve for 2 mg of uranium with 3 N H_2SO_4 (volume of resin = 2 ml; desorption rate 0.56 cm/minute).

First of all, it was necessary to find the conditions for separating 0.5-2.0 mg of uranium from accompanying elements. We used a column 28 cm long and 0.6 cm in diameter. The particle size was 0.25 mm, while the rate at which the solution was passed through the column was 0.3 ml/minute; the rate of desorption was 0.6 ml per minute.

It was found that it was sufficient to take 2 ml of sorbent in a swollen state. Under these conditions, it was sufficient to use 35 ml of 3 N sulfuric acid for complete desorption of the uranium. The curve for the desorption of 2 mg of uranium with 3 N H_2SO_4 is shown in Fig. 5.

A series of experiments was carried out on the determination of uranium in synthetic solutions containing various anions, 0.5-2.0 mg of uranium, and 50 mg iron (see Table 6). To the solution was added 0.45 g of EDTA-Na; it was then neutralized with ammonia until the appearance of a red-orange color (pH 5.5-6.5). The separation method was similar to that described above. The uranium was desorbed with 35 ml of 3 N H_2SO_4 and its content determined by titration with ammonium vanadate (0.004 N) (indicator – phenylanthranilic acid).

TABLE 6

Taken, mg		U found, mg	Error, %	Anion	Taken, mg		U found, mg	Error, %	Anion
U	Fe				U.	Fe			
0,5	50,0	0,49	−2,0	SO_4''	1,0	50,0	1,0	0,0	Cl'
1,0	50,0	0,99	−1,0	SO_4''	1,0	50,0	1,0	0,0	NO_3'
1,0	50,0	0,99	−1,0	SO_4''	2,0	50,0	2,01	+0,5	NO_3'
1,0	50,0	0,981	−1,9	Cl'	2,0	50,0	1,98	−1,0	SO_4''

TABLE 7

Taken, mg				U found, mg	U sorbed, %	Taken, mg				U found, mg	U sorbed, %
U	Fe	P	F			U	Fe	P	F		
1,0	50,0	1,0	—	1,0	100,0	1,0	50,0	—	1,0	1,0	100,0
1,0	50,0	2,0	—	1,0	100,0	1,0	50,0	—	5,0	1,0	100,0
1,0	50,0	3,0	—	0,99	99,0	1,0	50,0	—	10,0	0,99	99,0
1,0	50,0	10,0	—	0,981	98,1	1,0	50,0	—	20,0	0,68	68,0
1,0	50,0	20,0	—	0,867	86,7	1,0	50,0	—	50,0	0,56	56,0
1,0	50,0	50,0	—	0,641	64,1	1,0	50,0	—	100,0	0,37	37,0
1,0	50,0	100,0	—	0,471	47,2						

The mean relative experimental error was found to be within the permissible limits; uranium was completely separated from iron.

The effect of a number of anions on the sorption of uranium from solutions containing EDTA-Na on the cation exchange resin IRC-50 was also studied. The results given in Table 6 indicate that the ions Cl^-, NO_3^-, and SO_4^{2-} do not interfere with the sorption of uranium on the cation exchange resin. Phosphate and fluoride ions, at concentrations ≥10 times that of uranium, lower its sorption (Table 7).

The technique used for analyzing pure uranium ores was identical to that used for the synthetic solutions.* For the analysis of silicate ores it was sufficient to add EDTA-Na in an amount four times that of the aliquot of sample taken; for the analysis of iron ores or ores containing tenths of a percent of calcium, the amount of EDTA-Na taken should be 7-8 times the aliquot of sample. The results are given in Table 8.

TABLE 8

Ore No.	U content, %		Ore No.	U content, %	
	chromatographic method	specified content		chromatographic method	specified content
6	0,069	0,07+0,001	7	0,035	0,036 (hydrophosphate method)
	0,069			0,035	
	0,069			0,034	
	0,069		8	0,242	0,237±0,06
5	0,208	0,22±0,01		0,242	
	0,211			0,244	
	0,213		9	0,313	0,325±0,009
	0,211			0,31	
	0,206			0,313	

In uranium solutions, the main mass of the dry residue is composed of calcium and sodium salts, while the uranium content varies from one to a hundred milligrams per liter. As a result, before effecting separation by a chromatographic method, it is necessary, first of all, to enrich the sample by coprecipitating the uranium on ferric hydroxide. The requisite volume of solution depends on the uranium concentration.

TABLE 9

Solution No.	Content of U, mg				Deviation from the true value, % (relative)
	chromatographic method		ether extraction		
	in the sample	in a liter	in the sample	in a liter	
1	0.72	2.9	0.75	3.0	−3.3
	0.735				
	0.726				
	0.726				
2	1.604	161.2	1.65	165	−2.3
	1.604				
	1.62				
	1.62				

It was found possible to determine uranium in synthetic solution No. 1 (3 mg/liter uranium) and in the soda solution No. 2 (165 mg/liter uranium).

To a sample of solution was added 10 ml of concentrated HNO_3, the solution was boiled for 15 minutes to remove carbon dioxide, and then 1 ml of a 5% solution of $Fe_2(SO_4)_3$ added; the ferric hydroxide was precipitated with ammonia solution. The precipitate was filtered off and dissolved on the filter in a hot 1 N acid solution (HNO_3, HCl), 1 g of dry EDTA-Na was added, and the procedure described for the analysis of uranium ores subsequently followed.

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*The samples were decomposed in the usual way.

The results are given in Table 9.

SUMMARY

Ion-exchange chromatography can be used for separating uranium from accompanying elements, use being made of differences in the capacity of uranium and the other elements to form compounds with EDTA-Na.

Separation is possible in two cases:

in acid media, in which uranium is found in the form of a positively charged ion, most of the accompanying elements form an anionic complex with EDTA-Na and are not sorbed by a cation exchange resin;

in media which are almost neutral, in which uranium is found in the form of an unstable anionic complex, and can be sorbed by carboxyl resins after decomposition of this complex.

Two variants are used depending on the nature and amount of accompanying elements:

removal of uranium from solutions with pH 1.7-1.9 on KU-2 cation exchange resin in the sodium form; this is applicable to materials which are rich in uranium;

removal of uranium from solutions with pH 5-8 on a cation exchange resin of the Amberlite IRC-50 type, in the sodium form; this variant is applicable to both rich uranium ores and to poor ores and poor uranium solutions.

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NEW METHODS FOR THE DETERMINATION OF VERY SMALL AMOUNTS OF OZONE

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The ever-increasing interest in determining small amounts of ozone is connected with the problems of studying the upper layers of the atmosphere, with the use of ozone as a highly active oxidizing agent in technics, and with the control of the atmosphere in production establishments on account of the appreciable toxicity of ozone. Despite the high reactivity of ozone and despite its reaction with various organic and inorganic materials, there is, as yet, no reliable method for its determination.

We have developed highly sensitive analytical methods which are based on the extinction of fluorescence and on the changes in color of indicator tubes on passing air containing very small amounts of ozone through them.

On the basis of published data on the interaction of ozone with fluorescein and a number of organic dyestuffs, we decided to study the possibility of using them for determination of small amounts of ozone [1-3]. Having established in the first few experiments that when the reaction is carried out in solution it only leads to a negligible effect, in our subsequent work we used solid chemisorbents, finely ground silica gel being impregnated with the appropriate reagents. Of the large number of fluorescent materials that we tested, the most sensitive to ozone were luminol and fluorescein, while, of the organic dyes, the most sensitive was fuchsin. "MSK" silica gel with a particle size ranging from 180 to 250 μ was, first of all, treated with 6 N hydrochloric acid; it was then washed with water until the washings gave no test for chloride ions, and, finally, calcined at 750°; silica gel treated in this way was impregnated with dilute solutions of the reagents indicated.

Preparation of indicator powder based on luminol. 0.025 g of luminol was dissolved in 25 ml of 0.1 N NaOH in a 100-ml standard flask and the volume made up to the mark with distilled water. 1 ml of this solution was transferred into another 100-ml standard flask and diluted with water to the mark. 2.0 ml of this dilute luminol solution was used for impregnating 1 g of silica gel. After careful mixing, the treated silica gel was dried for one hour at 100°.

Preparation of indicator powder based on fluorescein. 0.04 g of fluorescein was dissolved in 1 ml of 10% KOH and the volume made up to 100 ml with water. This solution was diluted 20 times with water to give the solution finally used for impregnating the silica gel; 1 g of silica gel was impregnated with 1.6 ml of the fluorescein solution; it was dried in a drying oven for one hour at 100°.

Preparation of indicator powder based on fuchsin. 0.01 g of fuchsin base was dissolved in 20 ml of alcohol in a 100-ml standard flask and the volume made up to the mark with water. The working solution was prepared by taking 6 ml of the original solution and mixing it with 5 ml of water and 1 ml of 0.01 N HCl. 1.6 ml of this solution was used for impregnating 1 g of silica gel; the silica gel was finally dried at 100° for one hour.

Glass tubes (45 mm long and 2.5 mm in diameter) were packed as tightly as possible with these sorbents; air containing known amounts of ozone was subsequently sucked through these tubes.

In order to prepare gas-air mixtures with low ozone concentrations, individual portions of ozonized air were introduced into evacuated pipets (100-50 ml). The gas mixture was transferred from the pipet into an 8-liter bottle with a ground-glass stopper, a small vacuum having been created beforehand in the bottle. The gas-air mixture was kept for several hours and the ozone content then determined iodometrically [4]. Sampling of test air

TABLE 1

The Relation Between the Length of the Treated Zone of the Indicator and the Amount of Ozone

Luminol			Fluorescein			Fuchsin		
ozone, γ	length, mm	ozone, γ per mm (coefficient)	ozone, γ	length, mm	ozone, γ per mm (coefficient)	ozone, γ	length, mm	ozone, γ per mm (coefficient)
0,8	5	0,16	1,5	5	0,30	1	3	0,33
0,9	6	0,15	1,5	4	0,38	1,75	4,5	0,40
1,1	6	0,18	1,7	5	0,34	1,95	5	0,39
1,27	12	0,11	1,75	5	0,35	2,0	7	0,28
1,6	13	0,12	3,0	9	0,33	2,56	5	0,44
1,7	11	0,15	3,2	9	0,35	3,5	9	0,39
1,75	10	0,17	3,2	10	0,32	4,0	12	0,33
2,2	10,5	0,21	3,4	9	0,38	6,4	15	0,43
3,2	27	0,12	3,5	11	0,32	8,0	19	0,42
	Mean	0,15	6,4	17	0,37	9,6	20	0,48
				Mean	0,34	10	23	0,43
							Mean	0,39

by sucking it through the indicator tubes was carried out while the inlet tube of the bottle was closed. After 0.5 ml of test air had been taken, the vacuum thereby created in the bottle was eliminated by allowing pure air dried by sulfuric acid to pass into it.

After treatment with ozone there is clearly observed in the luminol and fluorescein tubes, when examined under ultraviolet light, a section where the fluorescence has been extinguished, the length of this section being greater the higher the ozone concentration.

In the case of the luminol indicator, the extinction of the bright-blue fluorescence is accompanied by the formation of a dull, greenish color. The fluorescein tubes are decolorized by the action of ozone, and the decolorized part is deprived of its characteristic greenish-yellow fluorescence in the ultraviolet. The reaction of ozone with the fuchsin indicator is expressed by the formation of a blue-violet color – the length of the zone in which the color has changed being again proportional to the amount of ozone.

The relation between the length of the zone which has reacted and the amount of ozone taken was investigated in a series of experiments using known amounts of ozone. The results obtained are given in Table 1.

On the basis of the results obtained, calculating coefficients (conversion factors) were established for each of the chemisorbents; these conversion factors are expressed in terms of the amount of ozone (γ) corresponding to 1 mm.

As is evident from the table, the luminol indicator is more sensitive than the fluorescein and fuchsin indicators. When luminol tubes are used, 1 mm of extinguished zone corresponds to 0.15 γ of ozone; this is several times more sensitive than all methods of determining ozone hitherto known [5-7].

TABLE 2

Determination of Ozone in the Presence of Nitrogen Oxides

Ozone found, γ/liter	NO_2 found, γ/liter
0.14	1.7
1.5	5.3
1.58	1.0
1.84	5.3
6.5	5.5

Remembering that nitrogen oxides always accompany ozone, we studied the effect of nitrogen oxides on the determination of ozone by the indicators recommended [8-10].

Experiments with known concentrations of nitrogen dioxide showed that extinction of fluorescein, just like the change in color of the fuchsin indicator, only occurs when appreciable amounts of NO_2 are used. Of the indicators used, luminol was the least sensitive to nitrogen dioxide. Reaction with this indicator becomes appreciable at about 6 γ, that is, at a concentration 40 times that of the minimum amount of ozone that can be determined.

Fluorescein and fuchsin proved to be more sensitive to nitrogen oxides. In these cases, determination is only possible for amounts of NO_2 which are 13-6 times (respectively) that of ozone.

Ozone is determined as follows. The indicator tubes from which the caps have been removed are connected by one end to a small water or electroaspirator, and 1 liter of air drawn at a uniform rate in the course of 40 minutes through them. The tubes are examined under the light from a PRK-4 lamp and the boundaries of the extinguished zone marked; the length of the zone is then measured in mm in ordinary daylight. Determination of ozone by means of fuchsin tubes is based on the length of the blue-violet zone. In those cases where extinction of fluorescence or the change in color of the indicator has extended through the whole tube (this occurs at high ozone concentrations) the determination should be repeated, a smaller amount of test air being drawn through. Knowing the volume of air sucked through and the length of the zone in the indicator tube where reaction has occurred, the ozone concentration of the test air is calculated using the experimentally established conversion factors.

The methods which we recommend have been used for studying the gaseous composition of the air for various operating conditions of electrofilters designed for trapping dust.

Table 2 contains some results for the determination of ozone in the presence of nitrogen dioxide by means of luminol indicator tubes.

SUMMARY

Highly sensitive quantitative methods have been developed for the determination of ozone which are based on extinction of the luminescence of luminol and fluorescein.

A linear colorimetric method has been developed for determining ozone which is based on the change in color of silica gel impregnated with fuchsin solution.

It has been established that ozone can be determined in the presence of appreciable amounts of nitrogen oxides.

Of the indicators suggested, the one which is most sensitive to ozone, and least sensitive to nitrogen oxides, is an indicator based on luminol.

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RAPID METHODS OF MICROELEMENTAL ANALYSIS

COMMUNICATION 17. SIMULTANEOUS MICRODETERMINATION OF CARBON, HYDROGEN, MERCURY, AND HALOGEN ON ONE ALIQUOT OF ORGANIC MATERIAL*

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Methods for the gravimetric determination of carbon, hydrogen, and mercury based on a combination of elemental analysis with weighing of the mercury as a gold amalgam [1, 2] are inadequate and are, accordingly, not used.

Absorption of mercury by gold foil or wire, during decomposition of organic materials, has been used for its quantitative microdetermination by Boetius [3] and Korshun and Lavrovskaya [4]. We have used the rapid method of microdetermination of carbon and hydrogen in compounds described by Korshun and Klimova [5-8], the mercury being trapped by gold, so that these elements are determined simultaneously; the technique for combustion in a special case developed earlier was used for this purpose [9].

TABLE 1

Expt. No.	Weight of case + gold, mg*		
	before expt.	after passing 600 ml O_2 through	change in weight
1	4.840	4.828	−0.012
2	3.478	3.492	+0.014
3	3.800	3.790	−0.010
4	1.030	1.026	−0.004
5	8.750	8.730	−0.020

*The readings of the rider and the microscale are given without taking into account the tare.

The method consists essentially of subjecting an aliquot of material to rapid pyrolytic combustion, while the mercury is kept back in a quartz case containing gold, the case being located inside the combustion tube; the amount of mercury is determined by the change in weight of this case plus its contents. Carbon and hydrogen are determined as usual [5-8]. The same quantity of gold can be used for a long time, since it is readily freed from mercury as the latter accumulates by simply heating it in an air stream. During blank runs, and during combustion of materials not containing mercury, the weight of the case plus gold remains constant within the limits ±0.010-0.020 mg (Table 1); this ensures that mercury can be determined with an accuracy of 0.6-0.7% absolute.

If halogen is present at the same time, it too can be determined simultaneously with C, H, and Hg. For this purpose the products of pyrolytic combustion, after issuing from the test tube, pass first over heated silver in order to absorb the halogen and then over cooled gold, which traps the mercury.

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**Deceased.

In the same way, it is possible to determine sulfur, as long as the test material does not contain halogen as well as sulfur [10, 11]. Results for the simultaneous determination of C, H, and Hg, and also of C, H, Hg, and halogen or sulfur are given in Table 2.

TABLE 2*

Test material	Hg, %		C, %		H, %		Halogen and sulfur, %	
	found	dif.	found	dif.	found	dif.	found	dif.
$C_{11}H_{12}HgO$ 2-Methyl-4-phenylmercurbutine-3-ol-2	55,89	+0,29	36,86	+0,25	3,37	+0,02		
C—36,61%; H—3,35%; Hg—55,60%	55,63	+0,06	36,65	+0,04	3,34	—0,01		
$C_{18}H_{18}Hg$ Bis-(bicyclo[2,2,1]heptene-3-yl-ethinyl)-mercury	45,77;	—0,36	49,56	—0,15	4,14	—0,03		
C—49,71; H—4,17; Hg—46,13%	46,65;	+0,48	49,63	—0,08	4,28	+0,11		
$C_3H_3Cl_3Hg$ γ,γ'-dichlorallylmercury chloride	58,02;	+0,05	10,47	+0,06	1,00	+0,13	30,74	0,00
C 10,41%; H—0,87%; Cl—30,74%; Hg—57,97;	57,67	—0,30	10,54	+0,013	0,96	+0,09	30,84	+0,10
$C_{14}H_{14}Hg_4$ Tropilium mercurtetraiodide	22,60	+0,07	18,68	—0,20	1,55	—0,03	56,97	—0,04
C—18,88%; H—1,58%; J_4—57,01%; Hg—22,53%	22,34	—0,19	18,80	—0,08	1,56	—0,02	57,38	+0,37
$C_{20}H_{18}Br_2HgN_4$ Dimethylaminophenylmercur-4,4'-dibromdiazoaminobenzene	29,73	0	35,71	+0,12	2,68	—0,01	23,80	+0,12
C—35,59%; H—2,69%; Hg—29,73%; Br—23,68%	30,03	+0,33	35,58	—0,01	2,72	+0,03	23,61	—0,07
$C_{18}H_{16}HgN_2O_2$ Dimethylaminophenylmercur-4-nitrosonaphthol-1	40,46	—0,24	44,09	+0,24	3,27	0		
C—43,85%; H—3,27%; Hg—40 70%	40,83	+0,13	43,97	+0,12	3,31	+0,04		
$C_{22}H_{20}HgN_2O_2$ Dimethylaminophenylmercur-α-benzylmonooxime	36,40;	—0,41	48,39;	—0,09	3,84	+0,14		
C—48,48%; H—3,70%; Hg—36,81%	36,36	—0,45	48,53	+0,05	3,83	+0,13		
$C_{20}H_{18}BrHgN_5O_2$ Dimethylaminophenylmercur-4-bromo-4-nitrodiazoaminobenzene	31,72	+0,42	37,78	+0,30	2,99	+0,16		
C—37,48%; H--2,83; Hg—31,30%; Br—12,47%	31,52	+0,22	37,61	+0,13	2,82	—0,01		
$C_{22}H_{23}Hg_2N_3O_2S$ Bis-dimethylaminophenylmercur-benzosulfamide	50,30	0,00	33,43	+0,23	3,11	—0,03	4,12	+0,09
	50,10	—0,20	33,33	+0,13	3,03	—0,11	4,09	+0,06
C—33,20%; H—3,14% Hg—50,30%; S—4,03%								
$C_{14}H_6Br_8Fe_2Hg_5O_4$ The mercury derivative of cyclopentadienyl iron**	50,32	—0,02	8,44	0	0,59	+0,27	31,81	—0,29
C—8,44%; H—0,32%; Br—32,10%; Fe—5,61%; Hg—50,34%	50,14	—0,20	8,33	—0,11	0,58	+0,26	32,22	+0,12

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*All the analyses given in Table 2 were carried out with aliquots of 5-8 mg.

**5.46 and 5.40% Fe were simultaneously found in the same aliquots.

These examples do not exhaust the possibilities of simultaneous determination of mercury and other elements in organic compounds. For example, it might be expected that the various metals which are weighed in the form of their oxides could be simultaneously determined with carbon, hydrogen, and mercury, and sometimes even with halogen on the basis of the residue left after combustion of one aliquot. As an example, one can cite the analysis of the mercury derivative of iron cyclopentadiene, in which carbon, hydrogen, mercury, iron, and halogen were determined on one aliquot (Table 2).

It is particularly interesting to dwell further on the analysis of materials containing nitrogen. According to the observations of Boetius [3], during combustion of materials containing mercury and nitrogen in oxygen, high results are obtained for mercury as the result of the formation of a certain amount of mercury nitrate from the interaction of nitrogen oxides and mercury. Accordingly, Boetius recommends that combustion of nitrogen-containing materials be carried out in a current of an inert gas and that the nitrogen oxides be reduced with metallic copper inside the combustion tube. Boetius' method, like the modification of Korshun and Lavrovskaya [4], was developed on the basis of the principles of Pregl's classical microanalysis, with slow evaporation of the aliquot and quantitative oxidation of the vapors of the material by means of the oxidizing packing of the combustion tube. It is known that, under these conditions, the presence of nitrogen in the test material is conducive to the formation of appreciable amounts of nitrogen oxides [12, 13], trapping of which is absolutely essential in order to get correct results for the elemental analysis. It is otherwise in the case of rapid pyrolytic combustion, where the yield of nitrogen oxides, even during analysis of nitro compounds, does not exceed 12-14% of the total amount of nitrogen [7, 2]. In order to establish whether or not mercury nitrate is formed under the conditions used for rapid pyrolytic combustion of nitrogen-containing compounds, we carried out a series of combustions of picric acid in which a case containing gold, in which the mercury was found both in the form of an amalgam and as a film on the walls of the case, was placed inside the combustion tube. The change in the weight of the case after the experiments did not exceed the usual errors in weighing (Table 3). After these experiments, the case was washed several times with water, and the wash liquor tested for any nitrate ions by the reaction with diphenylamine. No nitrate ions were detected. Thus, we concluded that under our conditions no mercury nitrate is formed. Determinations of carbon, hydrogen, mercury, and halogen in materials containing nitrogen in the oxidized form confirm this conclusion (Table 2).

TABLE 3

Expt. No.	Weight of case plus gold, mg*			Notes
	before combustion	after combustion	difference	
1	7.660	7.672	+0.012	5-6 mg lots of picric acid were burnt. The case contained 7-11 mg of mercury.
2	1.991	1.972	−0.019	
3	1.951	1.963	+0.012	
4	1.963	1.959	−0.004	

*The readings of the rider and the microscale are given without taking into account the tare.

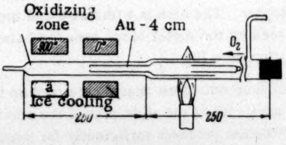

Fig. 1. Tube for determination of carbon, hydrogen, and mercury.
Key: (a) = MAG - 6R.

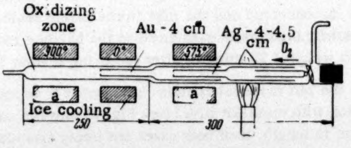

Fig. 2. Tube for determination of carbon, hydrogen, mercury, and halogen (or sulfur).
Key: (a) = MAG - 6R.

Apparatus. The apparatus is the same as that used for the simultaneous determination of C, H, and halogen in a case [9]. The arrangement of the case plus gold, the sample, and oxidizing zone is shown in Fig. 1. When the test material contains halogen, another case containing silver is also introduced into the combustion tube, as shown in Fig. 2. In this instance, the length of the wide part of the combustion tube should be not less than 30 cm. For rapid cooling of the absorption apparatus and of the case, we use in our laboratory metallic blocks with indentations corresponding in size to the Pregl apparatus and the case (Figs. 3 and 4).

Reagents. Thin gold wire or foil is used for trapping the mercury. Halogen is trapped with silver metal in the form of a mesh, foil, or wire weighing about 3 g. Silvered pumice cannot be used in this case because it traps part of the mercury and the results obtained for mercury and halogen are incorrect. The other reagents are are the same as those used for the determination of carbon and hydrogen [5-11].

Analytical procedure. We shall only deal with the techniques connected with determination of mercury and the positioning of the case and the test tube in the combustion tube, since that part of the method dealing with the determination of carbon, hydrogen, and halogen remains unchanged [9].

Before using a case, it is boiled in 1:1 HCl for ten minutes; it is then washed, dried, and finally calcined in the combustion tube. A layer of gold 4-cm long is placed in the calcined case (in its narrow part). The gold should be packed loosely so that it does not offer any resistance to the gas flow. The case plus gold are weighed, using a tared flask containing lumps of glass. Before starting an analysis, a blank test is run in which the case is placed in the combustion tube as shown in Fig. 1. Should the case already contain mercury absorbed during previous runs, then during the blank, as well as during combustion, the gold layer must be cooled with ice so that very small particles of mercury are not carried outside the limits of the case by the stream of hot oxygen issuing from the heated combustion tube. During the combustion of mercury-containing compounds, the case together with the small tube containing the sample (5-8 mg), is moved into the combustion tube to a distance of not less than 5 cm from the oxidizing zone, the oxygen throughput is adjusted to 30-35 ml/minute, and combustion of the test material is commenced with a gas burner. When combustion is complete, the wide part of the case is calcined with the burner. The narrow part should not be heated, so as to avoid evaporation of the mercury which has accumulated there. It should be noted that the mercury only partially falls onto the gold. Part of it settles on the cold walls of the narrow part of the case in the form of a very fine grey layer. When combustion has finished, the burner is extinguished and the cooling stopped, while the oxygen continues to pass for ten minutes through the combustion tube. During this period the aliquot for the next determination is taken. The absorption apparatus is disconnected and the tube immediately sealed with a stopper. The case is withdrawn and the tube removed from it, the case is transferred to the balance room and placed on the metal block near the balance (Fig. 4); it is weighed 25 minutes after removing it from the combustion tube [9].

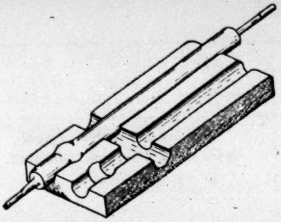

Fig. 3. Metal block for cooling the absorption apparatus.

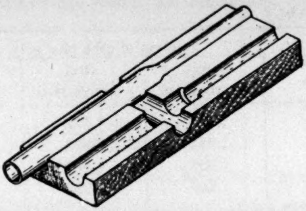

Fig. 4. Metal block for cooling the case.

When the test material contains halogen, it is necessary to introduce one more quartz case packed in its narrow section with metallic silver (see Fig. 2) into the combustion tube. When the wide part of the combustion tube is 30 cm in length, then both cases are freely arranged and combustion proceeds sufficiently far from the rubber stopper. It is of particular importance to ensure that all the silver layer is heated to 575° and that the mercury cannot be held back on the colder ends of the layer in the form of a silver amalgam. Combustion is carried out as described above. When combustion is complete, the burner is extinguished, the oven in which the silver is located is removed, and oxygen passed through for a further ten minutes; for the first five minutes, the cooling is continued, while for the second five minutes, the ice is removed. The cases containing the silver and gold are weighed, 25 and 30 minutes, respectively, after their removal from the combustion tubes.

It is recommended that the gold be regenerated at the end of each working day. For this purpose, the case is placed in a clean quartz tube with drawn-out ends, the tube is connected through a small washer filled with 1:1 nitric acid, to a Mariotte flask or to a water pump, and air is sucked through the tube while the gold is heated with a burner or an oven. When all the mercury has been driven off the surface of the gold, and, accordingly, from the case, the latter is removed and the tube washed with nitric acid.

SUMMARY

A method has been developed for the simultaneous microdetermination of carbon, hydrogen, mercury, and halogen in organic compounds; it is based on the pyrolytic combustion of the organic material, and the gravimetric determination of the four elements. Carbon, hydrogen, and halogen are determined by a method described earlier, while the mercury is trapped in the combustion tube in a special case filled with gold, and is then determined from the increase in weight of the case. The deviation of the experimental results obtained for mercury from the theoretical values does not exceed 0.6-0.7% absolute.

It has been shown that it is possible to determine mercury in materials containing nitrogen, and it has been demonstrated that, under pyrolytic combustion conditions, no mercury nitrate is formed.

It has been shown that when a test material contains a heavy metal which does not give volatile salts with a halogen, the metal can be determined simultaneously with carbon, hydrogen, mercury, and halogen.

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SEPARATION OF THE LOWER ALIPHATIC ALCOHOLS BY MEANS OF PAPER CHROMATOGRAPHY AND THEIR QUANTITATIVE DETERMINATION

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The problem which confronted us was to develop a method for separating mixtures of the lower aliphatic alcohols (methyl, ethyl, n-propyl, and n-butyl) which would be applicable to the analysis of the oxidation products of butane under conditions approximating critical conditions (temperature 145°, pressure 50 atmos.[1]). Quantitative separation and determination of alcohols is realized, in the main, by the method of separate oxidation of the alcohols in solutions freed beforehand from other oxidation products [2], while the difference in the solubilities of the alcohols in the aqueous and organic layer at various pressures is also used [3-6]. The drawbacks of these methods are the difficulties involved in carrying them out, the low experimental accuracy, and the impossibility of working with small amounts of materials.

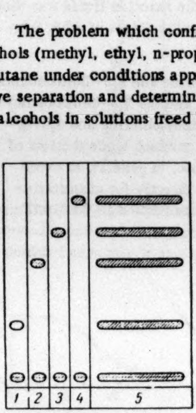


Fig. 1. Chromatogram of the 3,5-dinitrobenzoates of the lower aliphatic alcohols and their mixtures on acetylated paper. Mobile phase – heptane; stationary phase – methanol; t = 20°: 1) methanol; 2) ethanol; 3) n-propanol; 4) n-butanol; 5) mixtures of all four alcohols. The 3,5-dinitrobenzoic acid remains on the line on which the spots were placed originally.

The chromatographic separation of alcohol derivatives on silica gel [7-9] is complicated to carry out and is of low efficiency. Considerably more promising is the separation of the aliphatic alcohols by means of adsorption and partition chromatography on paper of their 3,5-dinitrobenzoic esters [10-12], 3,6-dinitrophthalates [13], alkylhydrophthalates [14-15], and also of their xanthogenates [16-18].

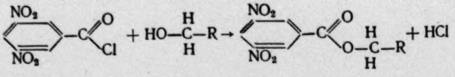
The 3,5-dinitrobenzoates of the alcohols yield the most reliable results. Other alcohol derivatives either demand preliminary careful purification of the test solution from organic compounds present in them, or the R_f values for the homologous series of alcohols differ too little from each other.

All published methods on the separation of alcohols by means of paper chromatography give only qualitative indications of the composition. We have developed a technique for the quantitative determination of aliphatic alcohols by this method. One of the basic difficulties which arises during development of a quantitative method is to achieve a constant, equal, and readily reproducible yield of the esters for all the alcohols. It is also necessary to choose conditions for the quantitative, selective determination of the isolated derivatives.

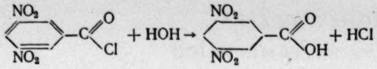
The method of isolating the 3,5-dinitrobenzoates from an anhydrous hydrocarbon medium [19, 20] required modification in order to apply it to the oxidation products of condensed butane, since the mixture contains a considerable amount of water (10-15%). Removal of moisture by extraction or by drying is impossible in the given instance, since this would lead to a large loss of alcohols.

The method used for preparing and isolating the 3,5-dinitrobenzoates was developed on the basis of synthetic mixtures of alcohols in a medium containing 15-20% of water and 80-85% hexane (or heptane).

To the mixture of alcohols was added 0.5 ml of pyridine and a saturated benzene solution of 3,5-dinitrobenzoylchloride. The amount of the latter added was determined on the basis that, in addition to the main reaction which leads to the formation of the ester:



there also occurs the side reaction,



leading to additional expenditure of 3,5-dinitrobenzoylchloride.

In order to ensure that the reaction goes to completion, the mixture was kept at 50-60° for 10-15 minutes in a round-bottomed flask fitted with a reflux condenser.

The reaction products partly dissolved and partly settled out as a precipitate. The reaction liquid was then poured into a measuring cylinder, while the precipitate remaining was washed with small portions of ether into the same measuring cylinder; the level of the latter was adjusted to 120 ml.

After all these operations, the test liquid contained some 3,5-dinitrobenzoylchloride and 3,5-dinitrobenzoic acid formed by hydrolysis of the latter in addition to the oxidation products, pyridine, and the 3,5-dinitrobenzoates of the alcohols. The method of washing the test solution free from 3,5-dinitrobenzoylchloride and 3,5-dinitrobenzoic acid by means of 1 N alkali solution [8] is not suitable for a quantitative method, since the loss of the 3,5-dinitrobenzoates that thereby occurs amounts to 20-25%. However, it is possible, in general, to avoid purification of the 3,5-dinitrobenzoates of the alcohols, and to use the reaction liquid directly for quantitative chromatography. The reason for this is that most of the chromatogram developers recommended in the literature for systems similar to ours only record materials containing a benzene ring with the two nitro groups in the meta position. Accordingly, under our conditions, only 3,5-dinitrobenzoylchloride and 3,5-dinitrobenzoic acid can interfere. Hydrolysis of 3,5-dinitrobenzoylchloride to the acid, on placing the solution on the paper and drying the spot, proceeds almost to completion. Thus, the only product which can interfere with the determination is 3,5-dinitrobenzoic acid. The latter remains on the paper on the spot where it is first placed ($R_f = 0$), consequently, for the quantitative determination of alcohols, it is possible to use a solution of their benzoates without any preliminary purification of these benzoates from the original reagents and other reaction products. The chromatograms were run on special paper type "Leningradskaya," this paper being acetylated beforehand [21, 22].

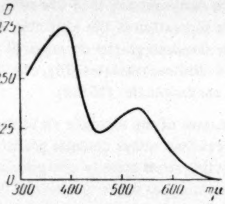


Fig. 2. Absorption curve of the 3,5-dinitrobenzoates of aliphatic alcohols.

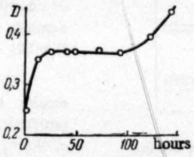


Fig. 3. Optical density of standard chromatograms of the 3,5-dinitrobenzoates treated with Yanovskii reagent stored for varying periods.

Absolute methanol was used as the stationary phase and hexane, heptane, or nonane as the mobile phase.

Ascending and descending chromatography gave equal results. In most experiments, ascending chromatograms were run, since the experimental technique involved is simpler.

The solution containing the 3,5-dinitrobenzoates of the alcohols was placed on acetylated paper 120 x 130 mm, in a thin band at a distance of 20 mm from the edge of the paper; the paper was then dried and placed in a chromatographic cell. The method of separation is described in the literature [10]. Good resolution of the bands was achieved on using 10^{-7} g-mole of the 3,5-dinitrobenzoates; larger amounts led to overloading of the paper, and resolution is not so good.

TABLE 1

R_f Values for the 3,5-Dinitrobenzoates of the Alcohols on Different Samples of Acetylated Paper

Batch No. of paper	Mobile phase	R_f (t = 20°, l = 280 mm) methanol	ethanol	propanol	n-butanol
I	Hexane	0.46	0.61	0.68	0.77
I	Heptane	0.36	0.50	0.63	0.67
I	"	0.32	0.50	0.61	0.71
I	"	0.32	0.54	0.60	0.72
I	Nonane	0.22	0.32	0.43	0.54
II	"	0.14	0.30	0.41	0.51
II	Heptane	0.19	0.33	0.44	0.52
II	Hexane	0.26	0.36	0.49	0.62
III	"	0.25	0.36	0.43	0.52
IV	Heptane	0.33	0.54	0.72	0.84

The developer used was Yanovskii reagent (4 g NaOH + 200 ml methanol + 400 ml acetone) which gives a blue-violet color when the solution contains compounds with two nitro groups in the meta position. This reagent has decided advantages over other developers, such as rhodamine Zh [10], alcoholic alkali [11], α-naphthylamine solution [23], stannous chloride in concentrated HCl with subsequent formation of azomethine compounds, etc., since formation of the colored compound is quantitative and the color obtained is fairly stable.

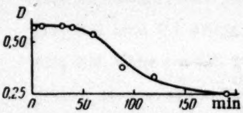


Fig. 4. Change in optical density of 3,5-dinitrobenzoates with time, after spraying them with Yanovskii reagent.

Qualitative detection of the alcohols. The arrangement of the alcohol derivatives on the chromatographic paper after development is shown in Fig. 1. The band of the 3,5-dinitrobenzoic acid remains at the spot on the paper where the solution was originally placed; there follows (from bottom to top) the bands for the 3,5-dinitrobenzoates of methanol, ethanol, n-propanol, and n-butanol. R_f values for the 3,5-dinitrobenzoates of the alcohols we are interested in have been given in [10]; they are: methanol 0.24, ethanol 0.39, n-propanol 0.46, and n-butanol 0.57. However, R_f values are not strictly constant values, and depend to a very considerable extent on the type of paper used. The R_f values found in the present work for different samples of acetylated paper are given in Table 1.

As these results show, there is a good agreement between the R_f values for one batch of paper, but when the paper is changed, the differences become significant. Because of this, a control spot of the 3,5-dinitrobenzoate of one of the alcohols is placed on each chromatogram alongside the band of a test mixture; this excludes the possibility of errors connected with variability in the R_f values.

Quantitative determination of alcohols. The individual 3,5-dinitrobenzoates of the alcohols isolated from their mixtures were determined on the basis of the absorption of the light by the colored compound formed on spraying the chromatograms with Yanovskii's reagent.

After development, the spots were cut out, treated with 20-ml methanol, and the optical density measured on a SF-4 spectrophotometer. The absorption curve of the compound formed is shown in Fig. 2. It has two absorption maxima at 385 and 535 mμ. Series measurements were carried out at 385 mμ.

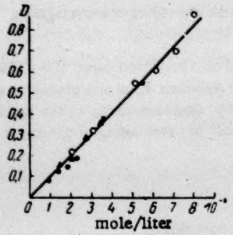


Fig. 5. Calibration curve: o) methanol; ▲) ethanol; ●) butanol.

Freshly prepared Yanovskii reagent is not suitable for quantitative determinations; the compound formed on development of a chromatogram has a lower optical density than the density obtained under the same conditions but using a reagent which has been allowed to stand for some time. The use of Yanovskii reagent which has been stored for a long time gives considerably higher optical densities as a result of the darkening of the reagent itself. As can be seen from Fig. 3, Yanovskii reagent, used after being stored for 24 hours, gives readily reproducible results in the course of the next 70-75 hours.

The colored compound formed on spraying is also unstable. However, as can be seen from Fig. 4, the optical density hardly changes at all 45 minutes after spraying. This time is quite sufficient for measurements.

The quantitative content of the alcohols was established on the basis of the optical density of the solutions using a special calibration curve. Such calibration curves were constructed for methanol, ethanol, and butanol for concentrations of $2 \cdot 10^{-4}$ to $8 \cdot 10^{-4}$ m/liter (Fig. 5). The optical density of the solutions obtained is directly proportional to the concentration of the alcohol and is the same for all three alcohols.

TABLE 2

Separation and Quantitative Determination of Normal Aliphatic Alcohols from Their Mixtures in Aqueous-Hydrocarbon Media

Alcohol, mole $\cdot 10^6$		Found, mole $\cdot 10^6$		
		Expt. 1	Expt. 2	Expt. 3
Methanol	8.24	8.40	8.20	8.50
Ethanol	5.60	5.35	5.70	5.52
Propanol	4.40	4.28	4.35	4.35
Butanol	3.58	3.52	3.54	3.50

TABLE 3

Quantitative Determination of Alcohols in Pure Heptane and in Heptane Containing 20% H_2O

Alcohol	Alcohol concentration (mole/liter)	D			
		heptane		0% C_7H_{16}+ +20% H_2O	
		1	2	3	4
Butanol	$2,24 \cdot 10^{-4}$	0,212	0,215	0,210	0,210
•	$5,37 \cdot 10^{-4}$	0,540	0,520	0,500	0,520
Propanol	$3,35 \cdot 10^{-4}$	0,340	0,340	0,350	0,328
Ethanol	$2,14 \cdot 10^{-4}$	0,220	0,210	0,180	0,210
•	$3,52 \cdot 10^{-4}$	0,330	0,350	0,360	0,345
Methanol	$7,21 \cdot 10^{-4}$	0,720	0,715	0,710	—
•	$8,24 \cdot 10^{-4}$	0,840	0,865	0,825	0,850

The proportionality between the optical density and alcohol concentration (within the limits 10^{-4} to 10^{-3} M/liter) shows that the yield of the alcohol derivatives, during all the stages of treatment, either approximates to 100%, or, even though it changes, is strictly proportional to the original concentration of the alcohol.

The method gives fully satisfactory results (Table 2); the experimental accuracy is equal to 1.5%.

In order to establish the possibility of using the suggested method for determining alcohols in hydrocarbon-water medium, and in a hydrocarbon medium, a series of experiments were made on synthetic mixtures. As is evident from Table 3, the yield of the esterified products is the same in all cases within the limits of experimental error. This means that water present in amounts up to 20% in the test solutions does not interfere.

The author wishes to thank N.M. Émanuél and Z.K. Maizus for their valuable advice in carrying out this work.

SUMMARY

A method has been developed for the chromatographic separation and quantitative determination of methanol, ethanol, propanol, and butanol in the form of the corresponding esters of 3,5-dinitrobenzoic acid. Quantitative determination of the alcohols is possible in the presence of water and other oxidation products of the hydrocarbon (butane).

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ANALYSIS OF MIXTURES OF ANILINE, MONO- AND DIMETHYLANILINE

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The analysis of mixtures of primary, secondary, and tertiary aromatic amines has been described in a large number of general textbooks and original papers [1-7]. In recent years, for nonaqueous mixtures of amines, new methods, mainly acidimetric, have been developed [8-11]. For the analysis of aqueous solutions of aromatic amines, we turned our attention to methods widely used in aniline-dye plants, according to which the total content of aniline and monoalkylaniline are determined on the basis of the nitrite used up in diazotization and nitration of the sample in the presence of Br^- ions, while the aniline content is determined separately by coupling the diazotized sample with a solution of β-naphthol added from a buret [12], or with a measured amount of R-salt, excess of which is titrated with a solution of p-tolyldiazonium chloride [13].

During a check on mixtures of pure aniline, monomethylaniline, and dimethylaniline, it was found that the accuracy of aniline determination by azo coupling is considerably less than the accuracy possible by diazotization. The errors in the determination of aniline and monomethylaniline, and also the high degree of skill required on the part of the analyst carrying out the azo coupling, led us to check on the acidimetric method of analysis in aqueous solutions.

Hantzsch [14] pointed out the strong basic properties of phenyldiazonium hydroxide long ago.

Cherkasskii [15] and Rostovtsev [16] later carried out potentiometric studies of solutions of diazonium chlorides and the completeness of the hydrolysis of these salts. Grachev [17] in a number of papers also made a potentiometric study of the structure and conversion of diazo compounds. The dissociation constant of phenyldiazonium hydroxide is equal to $10^{-3.1}$ according to I.V. Grachev (according to Hantzsch it is $10^{-2.9}$). A 0.5 N solution of phenyldiazonium chloride has a pH of 5.6. Bearing in mind that conversion of diazo solutions only occurs at higher pH values, one might expect a high degree of accuracy on titrating excess acid with alkali to the equivalence point of phenyldiazonium chloride.

During diazotization, one mole of aniline hydrochloride reacts with one mole of nitrite and one mole of hydrochloric acid to form phenyldiazonium chloride. Under the same conditions, nitrosation of monomethylaniline hydrochloride proceeds without additional expenditure of acid. Dimethylaniline hydrochloride, at not very high concentrations, hardly changes at all under the conditions used for analytical diazotization.

From the amount of acid which enters into the reaction during diazotization, it is possible to determine the amount of primary amine; while from the amount of nitrite used up, it is possible to determine total primary and secondary amines, and from the amount of acid used to combine with the amines up to the equivalence point, it is possible to determine the sum of all three amines.

Such an acidimetric determination of primary amine in a mixture of amines has not hitherto been used as an analytical method.

Analytical procedure. 1. Determination of the total amount of acid used for neutralizing the amines and excess acid. 20-30 g of the mixture of amines is dissolved in a 500-ml standard flask in 200 or 250 ml of 1 N hydrochloric acid; the solution is diluted with water to the mark. Let the amount of 1 N HCl used be N ml.

2. Determination of excess acid. To 50 ml of test solution is added 15 drops of a 0.1% solution of tropeoline 00, and the solution then titrated with 0.5 N NaOH using a reference solution (the pH of the solution is adjusted to

Analysis of Mixtures of Known Composition

Components	Composition, % wt.	Found, % wt.
Aniline	8.72	8.45
Monomethylaniline	79.48	79.7
Dimethylaniline	11.8	11.85
Aniline	8.72	9.5
Monomethylaniline	79.48	78.5
Dimethylaniline	11.8	11.85
Aniline	30	30.6
Monomethylaniline	60	59.3
Dimethylaniline	10	10.2
Aniline	51.6	51.9
Monomethylaniline	14.82	15.05
Dimethylaniline	33.55	34.6
Aniline	57.7	58.0
Monomethylaniline	27.1	26.8
Dimethylaniline	15.2	16.1
Aniline	19.15	17.7
Monomethylaniline	55.4	56.9
Dimethylaniline	25.4	25.2
Aniline	32.9	33.3
Monomethylaniline	23.55	23.0
Dimethylaniline	43.6	43.7
Aniline	31.1	31.1
Monomethylaniline	16.95	16.72
Dimethylaniline	51.6	51.6
Aniline	22.35	23.2
Monomethylaniline	50.65	49.7
Dimethylaniline	26.92	26.4
Aniline	23.6	22.5
Monomethylaniline	14.7	15.9
Dimethylaniline	61.7	62.2
Aniline	20.5	20.1
Monomethylaniline	10.3	10.6
Dimethylaniline	69.3	69.0
Aniline	30.4	30.1
Monomethylaniline	23.2	23.6
Dimethylaniline	46.4	46.2

Mean square errors: $\sigma_{\text{aniline}} = \mp 0.34$ ml, $\sigma_{\text{monomethylaniline}} = \mp 0.27$ ml, $\sigma_{\text{dimethylaniline}} = \mp 0.18$ ml, $\sigma_{\text{diazotization}} = \mp 0.12$ ml; $\sigma_{S_1} = \mp 0.23$ ml, $\sigma_{S_2} = \mp 0.4$ ml, where $S_1 = 0.2$ N−A and $S_2 = 0.2$ N−C.

$$\sigma_{S_2} > \sigma_{S_1}$$

2.55) containing the same amount of tropeoline 00 [18]. Instead of titrating with tropeoline 00, potentiometric titration of the solution to a pH of 2.55 can also be recommended. Let the amount of 0.5 N NaOH used be A ml (A should not be less than 5 ml).

If a hydrochloric aqueous solution of amines is being titrated, and not an anhydrous mixture, then after determination of excess acid, as just described, phenolphthalein solution is added and titration carried out with alkali to the color change. Additional expenditure of alkali with phenolphthalein should amount to 0.2 N−A ml.

3. Determination of nitrite used for diazotization of aniline and nitrosation of monomethylaniline is carried out by known methods [12, 13] on 50 ml of the solution prepared. Let the amount of 0.5 N nitrite solution used be B ml.

4. Determination of the amount of acid used up for diazotizing aniline. To 50 ml of the solution prepared is added about 2 g of sodium bromide, B ml of 0.5 N acid (the number of ml determined in 3), and then, with dropwise stirring, the same number B ml of 0.5 N nitrite. If (A−B) is greater than 5 ml, then there is no need to add acid. After two to three minutes, ice is added followed by about 20 g of chemically pure sodium chloride. The temperature drops rapidly to −5° to −7°. Ten drops of a 0.2% alcoholic solution of dimethyl yellow is added and the solution titrated with 0.5 N NaOH until the color changes from rose to yellow (without a reference solution). Let the amount of 0.5 N NaOH used be C ml.

Calculations:	Dimethylaniline content	(0.2−A−B)	60.5/d %
	Aniline content	(A+B−C)	46.5/d %
	Monomethylaniline content	(C−A)	50.35/d %

If, according to 4, B ml of 0.5 N acid was not added, then

Monomethylaniline content	(B+C−A)	50.35/d %
Aniline content	(A−C)	46.5/d %

Here, d is the weight of the test mixture.

The method was checked (see the table) on mixtures of aniline (setting point −6.1°), dimethylaniline (setting point −1.95°), and monomethylaniline, obtained by hydrolysis from benzosulfomethylaniline (m.p. 75-76°).

For high contents of dimethylaniline and for ratios of dimethylaniline to aniline in excess of 3:1, systematic errors arise from the expenditure of nitrite on nitrosation of the dimethylaniline. Nevertheless, as is shown in the table, the accuracy of an analysis of mixtures is sufficient for technical analyses. Potentiometric titration to the break on the titration curves showed that the error Δa, depending on the contents of the various amines, within the concentration limits set in the procedure, does not exceed 0.25 ml of 0.5 N alkali and 0.25 pH units.

SUMMARY

A fairly accurate and simple method has been developed for the analysis of mixtures of aniline, monomethylaniline, and dimethylaniline in aqueous solutions.

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A MICROMETHOD FOR THE DETERMINATION OF SUGARS BY MEANS OF THE COPPER COMPOUND OF TRIHYDROXYGLUTARIC ACID

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Earlier we described a method for the determination of reducing sugars by means of the copper complex of trihydroxyglutaric acid [1], which has an important advantage over methods based on the use of Fehling solution, since a strict proportionality is observed between the amount of univalent copper formed and the sugar present. The method suggested permits determination of glucose, fructose, and maltose with a high degree of accuracy. We found that this method can be used for the determination of microamounts of various sugars: glucose, fructose, galactose, xylose, maltose, saccharose, and also of glucose and saccharose in each others presence. In this case, again there is observed a proportionality between the amount of the sugar and the volume of permanganate solution used up in the titration.

The method permits determination of reducing sugars in various organic substances, e.g., in fruit juice, with a high degree of accuracy.

As tests showed, there is no need to purify technical trihydroxyglutaric acid specially [1].

EXPERIMENTAL*

The following solutions were used for the microdetermination of reducing sugars [1].

Solution No. 1. 40 g $CuSO_4 \cdot 5H_2O$ was dissolved in water, and the volume of the solution made up to 1 liter.

Solution No. 2. 128 g of trihydroxyglutaric acid and 207 g of sodium hydroxide were dissolved in water and the volume of the solution made up to 1 liter.

Experimental procedure. By means of a micropipet, n ml of the solution of the sugar (containing 0.1-9 mg of sugar) and 3-n ml of water was introduced into a series of test tubes. To these test tubes were then added 3 ml of solution No. 1 and 3 ml of solution No. 2. The test tubes were immersed in boiling water for six minutes, after which they were cooled with water to room temperature. The liquid was poured through a glass filter and the precipitate of cuprous oxide washed 2-3 times with hot, freshly boiled water. After the Bunsen flask containing the wash liquors had been replaced by a clean, small flask, the cuprous oxide was dissolved in 3-5 ml of ferric alum solution (containing 86 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$ and 108 ml of concentrated sulfuric acid per liter) and was transferred onto the filter. The test tube and the filter were rinsed 2-3 times with small portions of cold, freshly boiled water. The filtrate containing divalent iron was titrated in the flask serving as a receiver during the suction process, with 0.01-0.2 N potassium permanganate solution supplied from a microburet, until the color of the solution changed from green to a weak rose. The permanganate was standardized against a pure sugar (e.g., against chemically pure glucose).

When a series of experiments is carried out, the time taken to carry out an analysis is the same as for microdeterminations by the Bertrand method [2, 3]. The results obtained are given in the table.

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*R.A. Batyr took part in the work.

Sugar	Expt. No.	Taken, mg, $\underline{a}$	Found, mg, x_i	Found, mg (mean) $\bar{x}$	Dispersion s^2	Accuracy $t_{0,95}\cdot s_{\bar{x}}$	Probable relative error $\frac{s_{\bar{x}}\cdot t_{0,95}}{a}\cdot 100\%$
Glucose	1—9	1,00	0,996—1,004	1,002	$11\cdot10^{-6}$	0,0025	0,25
	10—18	3,00	2,990—3,012	3,002	$57\cdot10^{-6}$	0,0056	0,19
	19—27	6,00	5,991—6,008	5,999	$54\cdot10^{-6}$	0,0053	0,09
	28—36	9,00	8,976—9,012	8,995	$188\cdot10^{-6}$	0,0105	0,12
Fructose	1—9	3,00	2,993—3,009	3,003	$77\cdot10^{-6}$	0,0067	0,22
	10—18	6,00	5,995—6,019	6,005	$57\cdot10^{-6}$	0,0058	0,10
	19—27	9,00	8,980—9,997	8,992	$54\cdot10^{-6}$	0,0056	0,06
Galactose	1—9	3,00	2,991—3,006	3,001	$56\cdot10^{-6}$	0,0057	0,19
	10—18	6,00	5,998—6,012	6,006	$55\cdot10^{-6}$	0,0057	0,09
	19—27	9,00	8,989—9,003	8,995	$55\cdot10^{-6}$	0,0057	0,06
Xylose	1—9	3,00	2,992—3,005	3,001	$42\cdot10^{-6}$	0,0050	0,17
	10—18	6,00	5,998—6,012	6,003	$49\cdot10^{-6}$	0,0054	0,09
	19—27	9,00	8,989—9,003	8,997	$55\cdot10^{-6}$	0,0057	0,06
Maltose	1—9	3,00	2,982—3,002	2,998	$78\cdot10^{-6}$	0,0068	0,23
	10—18	6,00	5,984—6,026	6,003	$270\cdot10^{-6}$	0,0126	0,21
	19—27	9,00	8,986—9,007	8,993	$110\cdot10^{-6}$	0,0080	0,09
Saccharose*	1—9	3,00	2,995—3,008	3,002	$47\cdot10^{-6}$	0,0053	0,18
	10—18	6,00	5,992—6,005	6,001	$42\cdot10^{-6}$	0,0050	0,08
	19—27	9,00	8,989—9,001	8,993	$36\cdot10^{-6}$	0,0046	0,05

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* The saccharose was hydrolyzed by adding 2.5 ml of 10% hydrochloric acid to 50 ml of test solution and the mixture heated on a boiling water bath for 30 minutes. After cooling, the volume of the solution was made up to 100 ml.

Determination of saccharose in the presence of glucose. Solutions of glucose and saccharose were prepared containing 2.00 mg of the sugars per ml. The factor for permanganate, determined from nine determinations, was 1.832 on a glucose basis, and 1.635 on a saccharose basis.

2.18 ml of permanganate was used for titrating a mixture of 2.00 ml of glucose solution and 1.00 ml of saccharose solution before hydrolysis, while 3.40-3.42 ml of permanganate was used for titrating the same mixture after hydrolysis. The amount of saccharose found was 1.995-2.028 mg (mean of 9 determinations 1.999 mg).

During titration of a mixture of 1.00 ml of glucose solution and 2.00 ml of saccharose solution, 3.974-4.006 mg was found (mean of nine determinations was 3.992 mg as against 4.00 mg actually taken).

Determination of reducing sugars in grape juice by the method of additions. 10.00 ml of "Semil'on" grape juice was diluted to 1 liter.

6.265-6.302 mg of reducing sugar, calculated in terms of glucose, was found in 3.00 ml of juice. 2.095 mg of sugar was found in 1 ml, this value was the mean of nine determinations.

6.155-6.191 mg of reducing sugar was found in a mixture of 2.00 ml of juice solution and 1.00 ml of glucose (containing 2.00 mg). After subtracting the glucose, it was found that 1 ml of juice contained 2.088 mg of sugar (mean of nine determinations).

6.081-6.117 mg of reducing sugar was found in a mixture of 1.00 ml of juice solution and 2.00 ml of glucose solution; on subtracting the glucose it was found that 1 ml of solution contained 2.085 mg of sugar (mean of nine determinations).

Determination of reducing sugars in apple juice by the method of additions. 20.00 ml of apple juice was diluted with water to 1 liter.

2.309-2.345 mg of sugar was found in 1.00 ml of the juice solution by direct determination; the mean of nine determinations was 2.337 mg.

To 1 ml of the juice solution was added 2.00 mg of glucose. The amount of reducing sugar found was 4.324-4.361 mg; accordingly, 1 ml of the juice contained 2.344 mg of sugar (mean of nine determinations).

To 1 ml of the juice solution was added 4.00 mg of glucose. 6.304-6.340 mg of reducing sugar was found; therefore, 1 ml of the juice solution contained 2.328 mg of sugar (mean of nine determinations).

It follows from these results that the micromethod suggested permits accurate determination of the content of reducing sugars in fruit juices.

SUMMARY

A new micromethod is suggested for the determination of sugars by means of the copper compound of trihydroxyglutaric acid. The advantage of this method is the strict proportionality between the amount of sugar and the volume of permanganate used up in titrating the univalent copper formed.

The method permits determination of glucose, fructose, galactose, xylose, maltose, and saccharose with a high degree of accuracy.

The micromethod can be used for the accurate and rapid determination of sugars in fruit juices.

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*Original Russian pagination. See C.B. translation.

BRIEF COMMUNICATIONS

QUANTITATIVE DETERMINATION OF ZINC BY MEANS OF PRECIPITATION CHROMATOGRAPHY

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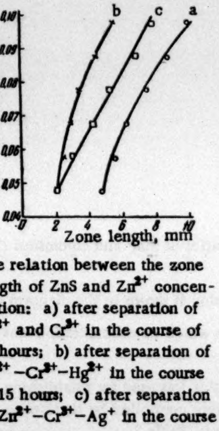
Precipitation chromatograms have clearly defined and even zone boundaries and an equal color intensity along the length of the zone. Under certain conditions, there is a definite relation between the length of the zone and the concentration of the material being chromatographed: the zone length expands with increasing concentration of the test material in solution [1, 2]. This made it possible to develop a method for the precipitation-chromatographic determination of the concentration of zinc ions in the form of its sulfide. Centrifuge tubes with a capacity of 10 ml and with a diameter of 12 mm at the cylindrical part were used for carrying out the precipitation-chromatographic experiments. All measurements were made in the upper, cylindrical part of the tubes. The carrier used was a 2% gel of agaroid [3] while the precipitant was sodium sulfide.



The relation between the zone length of ZnS and Zn^{2+} concentration: a) after separation of Zn^{2+} and Cr^{3+} in the course of 24 hours; b) after separation of $Zn^{2+}-Cr^{3+}-Hg^{2+}$ in the course of 15 hours; c) after separation of $Zn^{2+}-Cr^{3+}-Ag^{+}$ in the course of 24 hours.

As a result of preliminary experiments, it was established that the optimum ratio of carrier to precipitant is 5:2 (or 0.8 g of $Na_2S \cdot 9H_2O$ to 2 g of agaroid). (For this ratio the gel of agaroid has a pH of 10.)

The pH of the test solutions, as a rule, has no effect on the zone length.

0.5 ml or 1 ml of a solution with different concentrations of a zinc salt was placed on a prepared chromatographic column. It was established in the course of such experiments that the zone length increases linearly with increasing zinc-ion concentration of the solution [2]. However, it was also found that only 40% of the zinc, on an average, was precipitated from the solution in the gel.

Accordingly, in further experiments we tried to establish the conditions under which quantitative precipitation of zinc would be observed from the solution, while still maintaining the proportionality between the zone length and the concentration of zinc ions in solution. For this purpose, the effect of additions of solutions of chromium (III), mercury (II), silver, and lead (II) salts was studied, while the minimum zinc concentration which can still be determined with reasonable accuracy was also established. As a result of numerous experiments, the following technique was finally developed for the quantitative determination of zinc in the presence of chromium.

EXPERIMENTAL METHOD

A calibration curve was constructed by placing 0.5 ml (1 ml) of a zinc salt at various concentrations of 0.0476 M, 0.0576 M, 0.0676 M, 0.0776 M, 0.0876 M, 0.0976 M and 0.5 ml (1 ml) of 0.1 M $Cr_2(SO_4)_3$ on the agaroid gel containing the precipitant.

TABLE 1

Zone Length of ZnS for the Test Solutions

Solutions	Zn^{2+} concentration in solution, mole	Zone length, mm				
		1	2	3	4	mean
Known concentration (for constructing a calibration curve)	0,0976	10	10	—	—	10
	0,0876	8,5	9	—	—	8,75
	0,0776	7	8	—	—	7,5
	0,0676	6,5	6	—	—	6,25
	0,0576	5,5	5,5	—	—	5,5
	0,0476	4,5	5	—	—	5,75
Unknown concentration	X_1	8,5	8	8	8,5	8.25
	X_2	5,5	5	6	5,5	5,5
	X_3	7	7,5	7,5	7	7,25

Readings were taken after 24 hours. The chromium (III) zone was the same in all the tests (3.5 mm); the zones were clearly defined. The boundaries of the zinc zone were also sharp and even, the zone length being only dependent on the concentration. Qualitative reactions for zinc ions (in the solution above the gel) with dithizone and ammonium tetrathiocyanomercuriate gave negative results.

TABLE 2

Determination of Zinc Concentration by Titrimetric and Precipitation-Chromatographic Methods

Zn^{2+} solution	Zinc found, mole	
	by titration	by the precipitation-chromatographic method
X_1	0.0852	0.0845
X_2	0.0568	0.0575
X_3	0.0752	0.0760

Quantitative determination of zinc by the method indicated is possible for ratios of zinc and chromium (III), from equimolar solutions, equal to 1:1, 1:2, 1:10 by volume.

The curve relating the zone length to the zinc-ion concentration of the solution is shown in the diagram (a).

In order to check the method developed, zinc was determined in solutions in which its concentration was unknown; these were x_1, x_2, and x_3. The results are given in Table 1.

Using the results given in Table 1, a calibration curve was constructed, and this was used for establishing the zinc concentration of the test solutions: x_1, x_2, and x_3. The results obtained were controlled by titrimetric determination of the zinc with potassium ferrocyanide [4]. These results are given in Table 2.

During the quantitative determination of zinc in solutions of the ternary mixtures 1) $Zn^{2+}-Cr^{3+}-Hg^{2+}$; 2) $Zn^{2+}-Cr^{3+}-Ag^{+}$, thanks to the presence of the chromium, precipitation of zinc from solution proceeds quantitatively, while the relation between the length of the colored zone of ZnS and zinc concentration is also preserved. In these experiments again, to an agaroid gel containing Na_2S (in the proportion of 5:2) was added 0.5 ml (1 ml) of solutions of a zinc salt with the concentrations indicated above and 0.5 ml (1 ml) of a solution of 0.1 M $Cr(SO_4)_3$, and 0.5 ml (1 ml) of 0.1 M $AgNO_3$, or 0.5 ml (1 ml) of 0.1 M $Hg(NO_3)_2$. The relation between the zone length and the zinc concentration in the presence of the ions indicated is shown in the diagram (b,c).

SUMMARY

A quantitative precipitation-chromatographic method has been developed for the determination of zinc in the presence of trivalent chromium. The method is simple and requires only small amounts of test solution (0.5 to 1 ml).

The possibility has been demonstrated of determining zinc by the method indicated in solutions containing ternary mixtures: zinc-chromium-mercury and zinc-chromium-silver.

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DETERMINATION OF SMALL AMOUNTS OF BERYLLIUM BY MEANS OF β-DIKETONES

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Beryllium forms with β-diketones, acetylacetone derivatives, compounds which are very sparingly soluble in water [1]. It has been established that some of these diketones precipitate beryllium quantitatively. The present article contains a description of two methods for the gravimetric determination of beryllium by precipitating and weighing it in the form of its compounds with 2,2-dimethylhexanedione-3,5, $CH_3COOCH_2CO(CH_3)_3$ and 3-acetylhexanone-2, $CH_3COCH(C_3H_7)COCH_3$.

Saturated solutions of the diketones and a standard solution of beryllium sulfate with a concentration of 2 mg/ml Be were used for the work.

The method of precipitating beryllium with 2,2-dimethylhexanedione-3,5 consisted of the following. To the requisite amount of a saturated solution of the diketone, on the basis of 10-15 ml per mg of beryllium, pyridine was added until the pH was 5.5-6, and 0.2-0.3 ml of pyridine added in excess. The test solution of beryllium which had been diluted beforehand so that the beryllium concentration was 0.2-1.0 mg in 100 ml of solution was then added. After 5-10 seconds, a finely crystalline precipitate formed throughout the whole volume of the solution; after some time (1-1.5 hours), it collected in the form of coarse flocs on the bottom of the beaker, while the supernatant liquid became completely clear. The precipitate was then filtered through a No. 4 crucible and washed 4-5 times with distilled water; it was finally dried to constant weight at 50-55°.

Excess reagent does not interfere with the quantitative precipitation of beryllium; precipitation is better the lower the beryllium concentration of the solution.

TABLE 1

Precipitation of Beryllium with 2,2-Dimethylhexanedione-3,5

Be taken, mg	Precipitate obtained, mg	Be found, mg	Be taken, mg	Precipitate obtained, mg	Be found, mg
0,344	11,05	0,342	0,344	10,99	0,340
0,344	11,11	0,344	1,144	36,99	1,144
0,344	11,14	0,345	1,144	36,56	1,141
0,344	11,06	0,342	1,144	37,03	1,145
0,344	10,97	0,339	1,144	37,00	1,145

The concentration of the pyridine in the solution, which is necessary for establishing the requisite pH, did not usually exceed 0.5-0.7% by volume. Even a large excess of pyridine did not affect completeness of beryllium precipitation; however, too much pyridine in solution increases the time for the precipitate to coagulate. Ammonia solution cannot be recommended for adjusting the pH, since the results thereupon obtained are slightly low. This, apparently, can be explained by the low rate of formation of beryllium diketonate, as a result of which formation of the hydroxide occurs in parallel. Beryllium salts hydrolyze incompletely in the presence of pyridine, the hydroxide is not precipitated. Typical experimental results are given in Table 1.

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*Deceased.

2,2-Dimethylhexanedione-3,5 is not a selective reagent for beryllium, although the stability of its complex compound with beryllium is considerably higher than, for example, the stability of its compound with aluminum. All those elements which, under the conditions used for precipitating beryllium, form sparingly soluble compounds with the β-diketone, will interfere with beryllium determination. Magnesium does not interfere, since it forms a diketonate at pH $\gg$ 9, i.e., after completion of the formation of the beryllium diketonate. Beryllium can be separated from magnesium by precipitating the former at pH < 9. Beryllium, in amounts of 0.1-0.3 mg, can be determined with a high degree of accuracy in the presence of 100 mg of magnesium.

The method of precipitating beryllium with 3-acetylhexanone-2 is the same as that for 2,2-dimethylhexanedione-3,5, with the exception that, for the precipitation of each mg of beryllium, less diketone solution is used (3-4 ml) because of the higher solubility of this diketone. In addition, ammonia can be used for adjusting the requisite pH in this case. The experimental results are given in Table 2.

TABLE 2

Precipitation of Beryllium with 3-Acetylhexanone-2

Be taken, mg	Precipitate obtained, mg	Be found, mg
2.183	70.7, 70.4, 70.5, 70.7	2.186, 2.181, 2.183, 2.186
0.229	7.35, 7.38, 7.36, 7.40	0.227, 0.228, 0.228, 0.229
0.114	3.74, 3.72, 3.70, 3.71	0.116, 0.115, 0.114, 0.115

The methods described can be recommended for the determination of small amounts of beryllium of the order of 0.1-3.0 mg in solutions of its pure salts, or after separation of beryllium in a pure state from impurities. Under such conditions, these methods have a number of advantages over other gravimetric methods for beryllium, e.g., over the methods in which beryllium is precipitated as its hydroxide or phosphate. The small conversion factor to beryllium of 0.03096 in both cases, the low hygroscopicity of the precipitate, and the low temperature at which it is dried to constant weight are points in favor of this form of weighing beryllium rather than the gravimetric form BeO. The crystalline nature of the precipitate and the constancy of its composition distinguish it from beryllium phosphate.

SUMMARY

Two methods are described for the determination of beryllium in which it is precipitated and weighed in the form of its compounds with 2,2-dimethylhexanedione-3,5 and 3-acetylhexanone-2.

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A PHOTOMETRIC PICRATE METHOD FOR THE DETERMINATION OF NAPHTHALENE IN ITS MIXTURES WITH PHENOL

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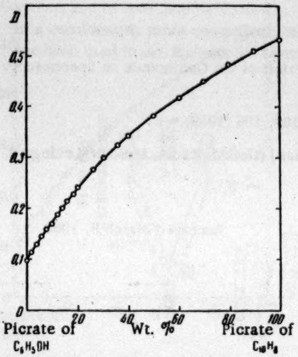
A spectrophotometric method of analyzing mixtures of phenol and naphthalene has been described in the literature [1]. As a consequence of the coincidence, in practice, of the characteristic frequencies in the absorption spectra of both components (273 and 275 mμ), the method presupposes the conversion of phenol into phenolate by the action of an alcoholic solution of alkali. The accuracy of this method, as the authors indicate, is about 4% [1].



We have developed a photometric method which is characterized by considerable simplicity and a high degree of accuracy. This method is the outcome of research carried out earlier [2], in which it was shown that, in the presence of aromatic hydrocarbons, the boundary of the absorption band of picric acid is shifted toward the long-wave part of the spectrum. The extent of this shift is determined by the character of the aromatic system and by the number of alkyl groups – substituents. During this work it was shown, for example, that the boundary of the absorption band of 0.1 M dichloroethane solutions of the picrates of benzene, its derivatives, and, in particular, of phenol is located in the region 412-425 mμ at an optical density of D = 1. Under the same conditions, the boundary of the absorption band of the picrates of naphthalene hydrocarbons is located at 455 mμ and higher. These solutions are characterized by a yellow color with varying intensity which means that it is possible to use a photometric method.

Weight % naphthalene	Optical density of solution of picrates, D	Naphthalene found, wt. %	Experimental error, %	Notes
7.6	0.149	6.9	−0.7	Melt
17.1	0.220	16.7	−0.4	Melt
22.3	0.250	21.5	−0.8	Mixture
22.4	0.248	21.2	−1.2	Melt
84.9	0.500	85.6	+0.7	Mixture

For this purpose, there is no need to use a quartz spectrophotometer; the determination can be carried out on any colorimeter – visual or photoelectric. We have carried out our work on an apparatus of the FÉK-M type using a blue light filter. The thickness of the absorbing layer is 20 mm.

Dichloroethane which had been washed several times with concentrated sulfuric acid until the latter ceased to acquire a color was used as the solvent. The dichloroethane was then carefully washed with water, dried with calcium chloride, and distilled [3].

EXPERIMENTAL METHOD

An aliquot of the test material (exactly 2 g) is dissolved in dichloroethane in a 100-ml standard flask; 5 ml of the solution obtained is mixed in the colorimeter cuvette with an equal volume of a standard solution of picric acid in dichloroethane, 100 ml of this solution contains 4 g of pure (recrystallized from alcohol) picric acid. Into a second cuvette, as a standard, is introduced 5 ml of the same solution of picric acid and an equal volume of pure solvent (in this way, the concentration of picric acid and of the picrates formed approximates to 0.1 M). The optical density of the test solution is measured and the naphthalene content corresponding to this optical density calculated from a calibration curve.

The calibration curve can be constructed with the aid of specially prepared mixtures of phenol and naphthalene, in which the weight of each mixture amounts to exactly 2 g. A curve of this type which we constructed is shown in the figure. Using this curve, we determined the naphthalene content of several of its mixtures or melts with phenol. The results obtained are given in the table.

The first part of the calibration curve (up to 20% by wt. of naphthalene) approximates to a straight line, as a result of which it is possible to establish the contents of the corresponding amounts of naphthalene not only graphically, but also by calculation:

$C = 140\ (D - 0.099)$ wt. % of naphthalene; here, 0.099 is the optical density of the phenol picrate solution.

The accuracy of the suggested method is determined by the error in preparing the solutions. The solvent can be recovered from used solutions by a double distillation. The absence of traces of naphthalene or phenol in the recovered solvent should be checked by the technique described.

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THE GLASS PARTS OF POLAROGRAPHIC APPARATUS

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The glass parts of polarographic apparatus – cells, capillaries, etc. – supplied with commercially available polarographs are not suitable enough. Even such an advanced apparatus as the Énergochermet TsLA recording polarograph [1] is provided with a cell with an internal (not isolated from the test solution) anode which does not have a jacket for thermostatting the apparatus. The capillaries supplied with this polarograph for the dropping electrodes do not enable one to use the apparatus to its best advantage. Actually, the large dropping period of these electrodes compels one to damp the apparatus; this leads to a sharp increase in the inertia of the following system and to considerable distortion of the shape of the polarographic curves. This had led us to publish details of a considerably more convenient, in our opinion, design for the glass parts of the polarograph, a design which has been used in our Institute for several years.

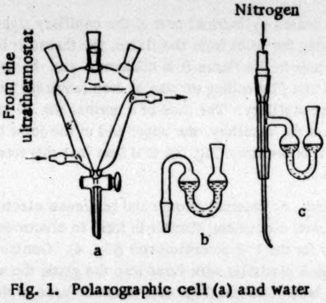

Fig. 1. Polarographic cell (a) and water seals (b and c).

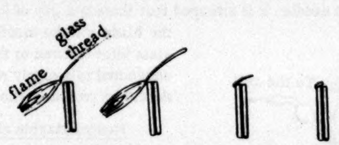

Fig. 2. The method used for fusing the blade onto the capillary tip.

The cell (Fig. 1a) is a conical vessel with a jacket which can be thermostatted by means of an ultrathermostat of the Heppler type or the TS-15 type. The lower, narrower end of the cell is provided with a tap for running off mercury or solution; the upper part of the cell has five inlets with normal ground-glass joints (NSh 10). The central inlet is for introducing the capillary of the dropping electrode, the two side inlets for the anode, and the reference electrode, the other for a capillary through which nitrogen is supplied, and, finally, the last inlet is used for introducing the test solutions, and is usually sealed with a water-seal (Fig. 1b), through which the nitrogen escapes to the atmosphere.

Sometimes – with the aim of freeing one inlet, e.g., for connecting a buret so that there is no access to atmospheric oxygen – it is necessary to connect the inlet and outlet for the nitrogen into one. In such a case, the capillary for the nitrogen is placed in the cell through a socket provided with a water seal (Fig. 1c). The cell is supported on a stand by placing it in a rubber ring stretched over a metal ring, a small piece of the latter being sawed out so that it is possible to slip the rubber tubing over it. In order to fix the cell firmly in position, a rubber bung is fitted onto the stem of the cell, and this bung is clamped in a boss and clamp-fitted to the same stand.

Dropping electrode. The most convenient type of electrode, both for analytical and research purposes, is a dropping electrode in which the drop is forced to drop off by coming into contact with a small blade [2]. The capillary of the electrode is prepared by drawing out a thermometer tube so that the length of the working (narrow) part amounts to 40-80 mm, while the diameter of the canal is 30-60 μ. The blade is fused on as follows. Air or nitrogen is passed continuously through the canal. The capillary tip, that part to which the blade is to be fused, is introduced into the small sharp flame of a blowpipe; simultaneously, into the flame is introduced a capillary tube of the same glass, drawn out beforehand into a thread (diameter about 0.1 mm) (Fig. 2a). As the thread softens (its tip starts to thicken) its tip is allowed to touch the heated cylindrical part of the capillary right at its end; the thread then sticks to the capillary. Without withdrawing the joint from the flame, the thread is bent; it is then drawn out, and finally fused (Fig. 2). By placing the blade in the flame it is thickened, and by means of a tungsten needle it is arranged that there is a gap of 0.5-1.5 mm (depending on size of drop required) between the blade and the mouth of the capillary. The core of a normal No. 10 ground-glass joint is fitted to the top of the capillary, the upper end of the joint being connected to a supply reservoir of mercury (Fig. 3); it is best that this reservoir should be provided with a tap.

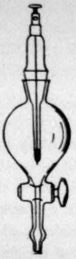

Fig. 3. Supply reservoir of mercury.

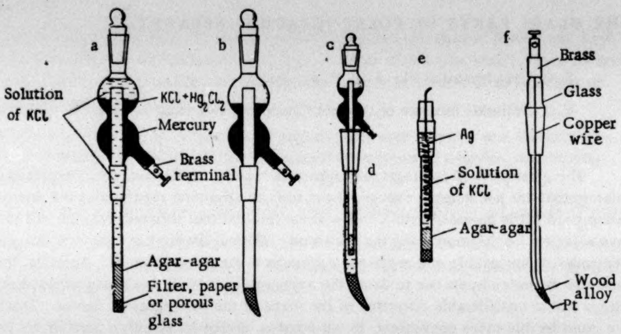

Fig. 4. Nonpolarizable electrodes and intermediate salt bridges.

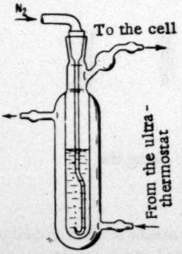

Fig. 5. Vessel for saturating the nitrogen with solvent vapor.

Nonpolarizable electrodes. As external anodes and reference electrodes, it is most convenient to use calomel electrodes, similar in form to electrodes prepared by the "Moskip" factory for the P-4 potentiometer (Fig. 4). Contact with the mercury is effected through a platinum wire fused into the glass; the wire is connected on the outside to a brass terminal (Fig. 4a), which is fused to the glass. The tip of the electrode siphon is sealed with a tightly rolled piece of filter paper and is filled with agar-agar gel and potassium chloride. In the reference electrodes the siphon is drawn out into a capillary, the end of which is placed close to the dropping electrode during measurements (Fig. 4b). On top, in the wide part of the electrode, calomel and KCl crystals are placed on top of the mercury. When it is desirable that the test solution should be free from chloride ions (e.g., when polarograms are taken at potentials more positive than that of the calomel electrode [3]) or potassium ions (when work is being carried out in the strongly negative potential region), then the nonpolarizable electrode is filled with mercury sulfate and potassium sulfate [3] or with tetrasubstituted ammonium salts. For potentiometric measurement of the potential of the dropping electrode with respect to the calomel electrode, or during work in such solutions, it is expedient to have a special calomel electrode with a narrow siphon (Fig. 4c), which is not placed directly in the cell, but through an intermediate salt bridge (Fig. 4d) of agar-agar, containing potassium sulfate (or nitrate) or tetrasubstituted ammonium salts, respectively. A bridge of this type can be used for preparing an external silver chloride electrode. For this purpose, a silver spiral or foil is inserted into it and the bridge filled with a potassium chloride solution (Fig. 4e).

When it is desirable to use a mercury pool as the nonpolarizable electrode, then a special electrode (Fig. 4f) is inserted into the cell instead of the external electrode, in order to establish contact with the mercury pool.

Vessel for saturating nitrogen with solvent vapor. Before the nitrogen is passed into the cell, it is necessary to saturate it with the vapors of the solvent used in the test solution at the experimental temperature. The vessel shown in Fig. 5 is suitable for this purpose. The nitrogen is bubbled through the solvent which is kept at the same temperature as the test solution. The jacket of the vessel is connected in series with the cell jacket, so that the vessel and cell are both thermostatted by means of the same ultrathermostat.

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*Original Russian pagination. See C.B. translation.

SOME IMPROVEMENTS IN THE MICROCRYSTALLOSCOPIC DETECTION OF POTASSIUM AS THE TRIPLE SALT POTASSIUM, COPPER, AND LEAD NITRITE

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Chernovitskii State University

Microcrystalloscopic detection of potassium on the basis of the formation of black cubes by the action of a solution of $Na_2CuPb(NO_2)_6$ permits detection of 0.15 γ K at a limiting dilution of 1:6600 [1]. The recommended procedure for preparing the reagent is to take 20 g of $NaNO_2$, 9.1 g of $Cu(CH_3COO)_2$, and 1.6 g of $Pb(CH_3COO)_2$ in 150 ml of distilled water acidified with 2 ml of 30% CH_3COOH. We tried to increase the sensitivity of detection, and to accelerate formation of crystals of $K_2CuPb(NO_2)_6$, by increasing the concentration of $Pb(CH_3COO)_2$ or $NaNO_2$ in the reagent. Solutions of the reagent, and of KCl of decreasing concentration, were placed dropwise on a glazed porcelain plate and the rate with which the crystals formed observed visually.

Tests showed that the $NaNO_2$ concentration, as one would expect, has a strong effect on the rate at which a precipitate appears, and on the sensitivity of potassium detection.

On using a reagent containing 25 g of lead acetate, 6.0 g of copper acetate, and 40 g of sodium nitrite, the limit of identification of potassium proved to be 0.9 γ K, when the reaction was carried out in a test tube, the limiting dilution being 1:1026. For microcrystalloscopic detection of potassium, a drop of the test solution was evaporated to dryness on a glass plate,after which a drop of reagent solution was added. The appearance of the characteristic crystals was observed at a potassium chloride concentration as low as 0.0025 M. The limit of detection was 0.9 γ K, while the limiting dilution was 1:10,300.

SUMMARY

By increasing the concentration of $NaNO_2$ and $Pb(CH_3COO)_2$ in the reagent used for detecting potassium [$NaNO_2$, $Pb(CH_3COO)_2$, and $Cu(CH_3COO)_2$], it is possible to increase the sensitivity of the microcrystalloscopic detection of potassium to 0.9 γ K; the limiting dilution is 1:10,310.

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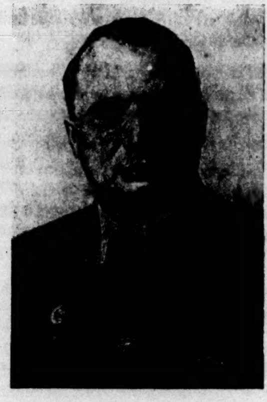
ALEKSANDR MAKSIMOVICH DYMOV

(ON HIS 60TH BIRTHDAY)

One of the directions taken by the scientific-technical activity of A.M. Dymov, particularly in the initial period, was the development of analytical methods for original raw materials, slags, and the finished articles of ferrous metallurgy, with their subsequent unification (standardization); this was the result of the acute demands of industrial chemical laboratories for such methods in connection with the restoration and development of Russian metallurgy and machine construction. As a result of this work, the Commission of the Soviet of industrial laboratories issued several collections of industrial methods of analysis (Chemical Analysis of Carbon and Alloy Steels, Cast Iron, and Ferroalloys, 1937; Standard Methods of Analyzing Cast and Steel, 1940; Collected Methods of Analysis of Cast Iron and Steel, 1944); the three were issued under the joint editorship of Academician É.V. Britske and A.M. Dymov. These collections proved of considerable help to industrial laboratories and to the development and improvement of the analytical chemical control of the metallurgical and machine construction industries.



In recent years (1953-1958), in the same field, A.M. Dymov has participated in developing international standards for analytical methods for manganese ores (he has been in charge of the work of the Soviet delegation of analysts at two international conferences in 1954 and 1956 which examined these standards).

In connection with the work on the standardization of analytical methods, together with his direct participation in their experimental development, A.M. Dymov compiled "Tables of Permissible Deviations in Experimental Results" for the appropriate elements, and has published a series of articles on the accuracy of chemical analytical methods which are applied to the control of metallurgical production, and for developing standard samples (standards) for increasing the quality (accuracy) of such control (the articles "The Accuracy of Methods of Analytical Control," 1937 and 1938; "Standard Samples and Their Part in Production Control," 1952).

A.M. Dymov's direct connection with industrial laboratories and his knowledge of their current demands are reflected in his published work. Thus, the books "Industrial Methods of Metallurgical Analysis, Rapid and Arbitrary," 1933, and "Technical Analysis of Ores and Metals" (which has reached five editions) have received wide recognition in industrial and scientific-research laboratories (the second book, which covers 50 pages, is a bench textbook in industrial and research laboratories; it has been translated into Chinese and Rumanian, and has been awarded a Stalin prize).

A.M. Dymov has paid special attention to the development of rapid (express) methods of analysis, the need for which has arisen from, and is arising from, improvements in technological processes (their intensification) in metallurgy and machine construction.

A.M. Dymov has developed and published several methods of this type ("A Rapid Method for the Determination of Silicic Acid in Alunites," 1930; "A Rapid Method for the Determination of Manganese in Bronzes," 1936; "Rapid Analysis of Ferrosilicon," 1937; "A Rapid Semimicro Method for the Determination of Calcium Oxide in Slags," 1946).

A.M. Dymov has also been interested in the questions of organizing industrial laboratories and in setting up chemical control of metallurgical production. He was a member of the technical commission set up by the chemical laboratories of the Magnitogorsk Metallurgical Combine, and of a commission for checking accepted methods of analysis, in connection with the starting of the first blast furnace (1931-1932). He published a number of articles on these questions including "A Giant of Socialist Industry — A Powerful Laboratory Base," 1932; "Laboratories for Industrial Enterprises," (in the paper "Izvestiya" 2, 1932); "The Role of the Central Industrial Laboratory," (in the paper "Tekhnika," 1932), and also articles devoted to experiments carried out abroad on the organization of industrial laboratories, and on accepted analytical methods (the article "Setting Up Production Control in German Industrial Laboratories," 1933, etc.).

At the first All-Union conference on analytical chemistry (1939) he read and published a report on the theme "The State and Organization of Analytical Control in Ferrous Metallurgy."

Another question which drew A.M. Dymov's attention was the training of qualified cadres of analysts, a question which hardly received any attention in pre-revolutionary Russia; he published a series of articles on this subject "Cadres of Analysts for Industrial Laboratories," 1954; "The Training of Personnel for Industrial Laboratories," 1938, etc. A.M. Dymov took part in organizing courses for training and improving the qualifications of analysts.

The articles "Industrial Laboratories in Capitalist Russia and Under the Soviet Government," and "Progress in Analytical Chemistry in the USSR in 40 Years," reflect the development of our industrial laboratories attached to the metallurgical and machine-constructing industries, and of analytical methods of control.

A.M. Dymov has developed physicochemical methods as well as classical methods and has introduced them into scientific-research work, and applied them to daily practice in industrial laboratories. He (together with co-workers) has developed and published a number of photocolorimetric methods for determining elements in iron alloys (nickel, cobalt, silicon, tungsten, lead); he has also published a polarographic method for determining iron, etc.

In recent years, A.M. Dymov and his co-workers have been developing methods for the determination of small amounts of elements and microimpurities in technical and pure metals. Mention may be made of the methods developed for the determination of low magnesium contents in modified casts and in metallic nickel of high purity, of arsenic and copper in metallic molybdenum, of magnesium, tungsten, and chlorine in metallic titanium, and of aluminum in carbon steels.

Several of the investigations he has carried out on developing analytical methods have been checked with the aid of radioactive isotopes (for example, the methods of determining phosphorus in ferroniobium and ferrotitanium).

It should be noted that the sequence in which A.M. Dymov developed methods for the determination of the components of iron and other alloys corresponds to the development of Russian metallurgy and machine construction in relation to the production of new brands of alloyed steel, ferroalloys, and the production of pure metals.

A.M. Dymov has written several textbooks. As long ago as 1929, he published A Textbook of Laboratory Technical Analysis, which went to five editions; in conjunction with members of the chair of analytical chemistry of the Moscow Steel Institute, he published a number of laboratory textbooks on quantitative analysis by a semimicro method. In 1959, A.M. Dymov published a textbook on the analysis of metallurgical slags, and is now preparing a textbook on the analysis of iron and manganese ores.

Mention must also be made of the large amount of work he has carried out in editing and reviewing textbooks and journals in the field of analytical chemistry and technical analysis.

A.M. Dymov is a member of the editorial board of the Journal of Analytical Chemistry USSR, and of Industrial Laboratories.

The Commission on Analytical Chemistry and the Editorial Board of the Journal of Analytical Chemistry, Academy of Sciences, USSR, wish A.M. Dymov many years of fruitful scientific work and success in educating the young generation for the good of our country.

CHRONICLE

PROGRESS IN ANALYTICAL CHEMISTRY IN CHINA

D.I. Ryabchikov

In 1952, a vast network of analytical laboratories was established in China in the specialized, reopened Institutes of the Academy of Sciences and Ministries and their branches in the provinces (in the chemical faculties), in the places of work of geological prospecting parties, and, later, even in the social communes. The chemical methods predominantly used initially for production control have, in recent years, been replaced by more accurate and rapid instrumental methods. Equipment is designed for small laboratory groups working on the analysis of mineral wealth. Massive preparations are being made for field laboratories.

During the development of enrichment schemes, and then for the technological treatment of the raw material, particularly for the production of nonferrous and rare metals, analytical control is used to a considerable extent. As a rule, all new industrial enterprises are provided with good analytical laboratories.

The importance of the analytical control of production and the quality of the finished products in all branches of industry and agriculture were clearly demonstrated in the All-Chinese Exhibition of Industry and Transport held in Peking toward the end of 1958, and in the Agricultural Exhibition held in January, 1959. At these exhibitions, there were shown examples of modern Chinese laboratory apparatus including: high-quality analytical balances, photocolorimeters, polarographs, spectrographs, various electrical heating equipment, glass and porcelain vessels, and a very large variety of reagents (up to 5000 items). All this has been produced on the bases of reconstructed industrial enterprises and experimental shops in scientific-research institutes and colleges.

The wide scope of analytical work in the country has demanded that the problem of cadres of workers be solved. Few analysts were trained in the small number of colleges of old China. In 1952, during the reforms that were carried out in the chemistry faculties of the universities, chairs of analytical chemistry were created. Training of analysts is now carried out in China in universities and in specially created educational establishments, at intermediate and higher levels, in chemical, geological, and metallurgical institutes of the Academy of Sciences. More and more analytical work is being started in the chairs of analytical chemistry and in the analytical laboratories of the chemical institutes of the Academy of Sciences. Of interest is the methodical work on developing simplified methods for the analysis of soils, fertilizers, cast, steel, copper, etc., for social commune laboratories.

The teaching laboratories of the chemistry faculties are well provided with the requisite equipment, apparatus, and reagents. The faculty libraries and the libraries of scientific-research institutes are well stocked with literature. Many Russian textbooks have been translated into Chinese. Fundamental foreign textbooks are photocopied after 2-3 months and pass into the country's libraries.

In connection with the development of new technics, methods have been developed and adopted for the determination of trace impurities in specially pure metals and compounds.

The classical methods of precipitation, coprecipitation, and the separation of the elements have been further developed in order to apply them to the concentration and determination of traces of inorganic components in the work carried out by En Jeng-ying (Peking University), Liang Shu-ch'uan (Institute of Chemistry of the Academy of Sciences), and Shu-shang (Institute of Applied Chemistry of the Academy of Sciences). Work has also started along the same directions on microchemical methods of analysis by Chung Yu-lan (Institute of Chemistry of the Academy of Sciences).

Ts'on Yung-hua at the Institute of Applied Chemistry of the Academy of Sciences, organized a group for carrying out polarographic analysis in Changchung; subsequently, soon after the liberation, Liu Ch'en-i carried on with this development, and three years afterward, the method became widely used in the country. Kao Siao-hsa carries out research on the theory of the polarographic method in Peking University. In recent years, work has started on oscillographic polarography. Work is being carried on in a number of institutes on developing new marks of polarographs. The chromatographic method has been widely used in recent years for separating complex mixtures, and for preparing the rare and rare-earth elements in pure form. Of special interest in this connection is the work directed by Ts'ung Huang-peng at the Institute of Applied Chemistry in Hangkung, and by Liu Ta-kang in the Chemical Institute in Peking. Success is being achieved in synthesizing ion-exchange resins, particularly in the chemical institutes and in the Institute of Applied Chemistry of the Academy of Sciences. Chromatography and electrochromatography on papers is being successfully carried out for the analysis of the rare earths, while, in Shanminsk University, Lu Ts'un lan and Huang Yü-ying have determined microamounts of the alkali metals by this method.

Spectrographic methods of analysis are particularly widely used in connection with the express analysis of steel and nonferrous metals. Research on spectroscopy is carried out at the Institute of Applied Chemistry of the Academy of Sciences in Changchung under the guidance of Hsueh-chou.

There are well-equipped laboratories for spectrographic analysis in a number of the institutes of the Academy of Sciences (the Institute of Geology and Chemistry in Peking; the Institute of Metallurgy and Ceramics in Shanghai; the Institute of Mining and Metallurgy in Chansha, and other institutes), in many other institutes, universities, and factories. Initially, the requisite apparatus was imported from the Soviet Union, the German Democratic Republic, and England; in recent years, however, production of spectrographs has been organized in China on the basis of models developed in the Institute of Optical Glass in Changchung.

In a short time, analytical chemistry has assumed in China an important part in solving practical problems in the most diverse branches of science and technics. A sound technical material basis has been developed, many analysts have been trained, and, with the interest shown by the Communist Party and the Chinese Government, analytical chemists are honorably struggling with the huge problems posed by the second five-year plan for the development of the social economy of China.

A NEW REAGENT FOR THE DETERMINATION OF SCANDIUM AND VANADIUM – "SULFONAZO"

A new reagent which has been designated "sulfonazo" has been synthesized at the All-Union Scientific-Research Institute of Chemical Reagents (IREA) for the photometric determination of scandium and vanadium.

The new reagent possesses several advantages over the reagents widely used at present for these cations; it is characterized by its high sensitivity and selectivity, and by the stability of the colored solutions it forms.

Organizations and enterprises who would like to test the new reagent may receive a free sample and instructions for its use on applying to the address of the Institute of Chemical Reagents (Moskva, Zh 33, Samokatnaya Ul; D.4a), so that they can, within two months of receiving the sample, report back to the Institute on the practical value of the reagent.

The Institute is willing to advise on all questions relating to the use of "sulfonazo."

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.– Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

A FLAME SPECTROPHOTOMETER ADAPTED FOR SPECTRA RECORDING AND ITS APPLICATIONS

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A flame spectrophotometer based on a type UM-2 monochromator [1, 2] or on an apparatus of the SF-4 type [3] is a universal apparatus, which permits determination of a large number of metals on the basis of the measurement of the intensity of the spectral lines of elements excited in the flame. When low concentrations of elements are to be determined, however, difficulties arise. In the first place, the flame itself serves as a source of background, which is determined by the excitation of radicals and OH, CH, and C_2 molecules. As a result of some instability in the background of the flame, it essentially limits the sensitivity and accuracy of the method; on working with the flame of a mixture of acetylene and air, the flame background is of significance for determination of elements whose lines are found in the 400-600 mμ region; in the red and infrared this background is negligibly small. Secondly, foreign elements present in the test solution often give radiation, the spectrum of which consists of molecular bands or is continuous. These elements include, in addition to the alkaline earth elements and the rare earths, boron, aluminum, copper, and phosphorus, the following elements as well [4] Mo, Nb, U, Zn (continuous radiation) and Be, V, Sn, Te, and Ti (band spectrum). The radiation of the foreign element increases the photocurrent and leads to a positive error. Finally, the spectral line of the test element may be located near the lines of the foreign element present in solution (e.g., the lines Mn 403.1, 403.3, and 403.4 mμ are located close to the lines K 404.4 and 404.7 mμ; and the line Ca 422.7 mμ is near the line Sr 421.6 mμ, etc.). When the apparatus does not have sufficient dispersive power and wide slits are used, the radiation of the foreign element, when the latter is present in high concentrations, is superimposed on the radiation of the test element, so that high results are obtained for the latter.

In order to eliminate errors caused by radiation from foreign elements, it is usually recommended that the background be measured at the base of the analytical line, and that this value be subtracted from the reading of the photocurrent of the test line. Such a technique, however, does not yield accurate results at low concentration of the test element and high concentrations of the foreign elements. When the foreign elements have complex molecular spectra, it is difficult, in general, to apply corrections for the background, because of the indeterminacy in finding the exact position of the base of the line, and the inevitable "dead path" of the drum used for rotating the monochromator prism. As observations have shown, the effect of the background can be taken into account more accurately by using a recording spectrophotometer in which the spectra are scanned [5, 6]. We have used an apparatus of this type for developing a method of determining La, Eu, Yb, and Y in the sum of the rare earth oxides [7]. In the present article we shall dwell further on some other instances of the use of such an apparatus.

Apparatus and Experimental Technique. A flame spectrophotometer based on the UM-2 type of universal monochromator, and described earlier [1, 2] was used; to this instrument was added a mechanism for rotating the prism drum, and an electronic recording potentiometer. The rotating mechanism is shown in Fig. 1. An iron plate 1 is fixed to the base of the monochromator by means of bolts, a motor whose rotor turns at the rate of 47.5 rps was fixed onto this plate. By means of a multistage reducer 2 and cog 4, the rotation of the motor axis was transmitted by spindle 3, arranged on the drum axis; this spindle gave one turn in six minutes (5 min 46 sec) during the operation of the motor. A bushing provided with two spindles 5 was fitted onto spindle 3; the bushing

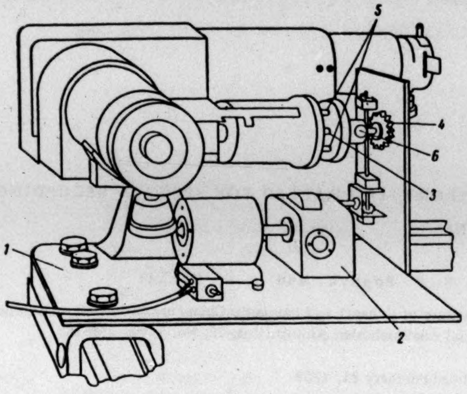

Fig. 1. UM-2 monochromator with a mechanism for rotating the prism drum.

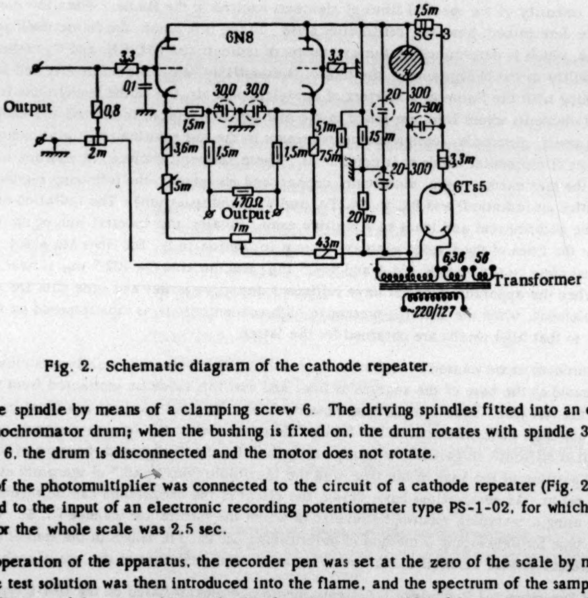

Fig. 2. Schematic diagram of the cathode repeater.

can be fixed on the spindle by means of a clamping screw 6. The driving spindles fitted into an ebonite disc fixed into the monochromator drum; when the bushing is fixed on, the drum rotates with spindle 3, while on dropping out the screw 6, the drum is disconnected and the motor does not rotate.

The anode of the photomultiplier was connected to the circuit of a cathode repeater (Fig. 2), the output from which was fed to the input of an electronic recording potentiometer type PS-1-02, for which the time of flight of the pen for the whole scale was 2.5 sec.

During the operation of the apparatus, the recorder pen was set at the zero of the scale by means of the potentiometer, the test solution was then introduced into the flame, and the spectrum of the sample recorded in the region where the line of the test was located. For the chosen slit widths of 0.1 or 0.05 mm, the time in the course of which the image of the line becomes completely visible through the outlet slit, during rotation of the drum, is 8-9 seconds, and, since the recorder pen has a shorter time of flight, 2.5 sec altogether, the value of the photocurrent of the line is recorded correctly. It is best that the outlet slit should be greater than the inlet slit, e.g., the outlet slit should be 0.1 mm and the inlet slit 0.05 mm; in such a case the light from the image of the line will pass out of the slit in a certain time interval during rotation of the drum.

TABLE 1

Deviations during Recording of the Lithium Line in the Presence of Sodium (50 mg NaCl/ml)

Lithium concentration, µg/ml	No. of recordings of the line	Mean height of the line, mm	Deviation from the mean value of a single recording		
			max	min	mean
0,1	7	8,5	15,1	3,8	8,9
0,2	7	18,2	12,3	0,8	6,0
0,5	6	49,7	10,2	2,5	6,4
1	5	76	7,6	0,8	3
1	6	32	5,0	0,0	2,5
5	6	93	1,4	0,3	1

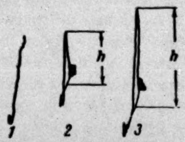

Fig. 3. Recording of the Li 670.8 line 1) NaCl solution, 50 mg/ml, free from lithium; 2) NaCl solution, 50 mg/ml + + 0.1 µg Li/ml; 3) NaCl solution, 50 mg/ml + 0.2 µg Li/ml; h is the height of the lithium peak.

After recording the spectrum of the test sample, the spectra of standard solutions or of solutions of the test sample to which known amounts of test element have been added are recorded, and the content of the element determined by the comparison method or by the method of additions. In the experiments described below, the flame of a mixture of acetylene and air was used; the monochromator slits used were: inlet slit 0.05 mm (slit height 6 mm), outlet slit 0.1 mm. Two photomultipliers were used: FÉU-19 for working with elements whose lines are located in the visible part of the spectrum, and FÉU-22 for working in the infrared (for Rb determinations).

The voltage applied to the photomultiplier was such that the line being measured photometrically gave a recording several cm long or the maximum possible. The paper ribbon moved at the rate of 360 mm/hour (6 mm/min).

The experimental accuracy depends on the ratio of the values of the background and the recorded peak of the line. It was determined for lithium by successive recordings of the peaks given by its line for solutions with varying concentrations. The mean values of the measured heights of the line were taken, and the deviation from this mean calculated in individual cases. The results obtained are given in Table 1.

As is evident from Table 1, when the height of the recorded line is sufficient, a higher experimental accuracy can be achieved than is possible with an apparatus in which galvanometer readings are taken. Thus for a content of 5 µg of Li/ml, the maximum deviation from the mean is 1.4%, while the minimum deviation is 0.3%; at the same time, the normal accuracy for visual readings is 2-4%.

Determination of Lithium in the Presence of Predominating Amounts of Sodium. Such a determination may be of importance, for example, during the determination of traces of lithium in rock or natural table salt for geochemical work. A salt solution with a concentration of 50 mg/ml was prepared and the spectrum of the sample recorded from 660 to 686 mµ (50 drum divisions) in the course of 50 sec. For comparison the spectra of standard solutions were recorded; these solutions contained the same NaCl concentration while Li was added in various amounts to give concentrations of 0, 0.1, 0.2, 0.5, and 1.0 µg/ml. Smoked glass was placed in front of the FÉU-19 photomultiplier cathode so as to absorb sodium radiation 589.0-589.6 scattered in the monochromator. The voltage applied to the photomultiplier was such that a solution to which 0.1 µg of Li had been added per ml gave a sodium peak of about 1 cm during recording of the lithium peak.

Examples are given in Fig. 3 of the spectra obtained and of the method of determining the peak height of lithium. As is evident from this figure, Li can be determined at concentrations as low as 0.1 µg of Li/ml, or 0.0002% in the sample.

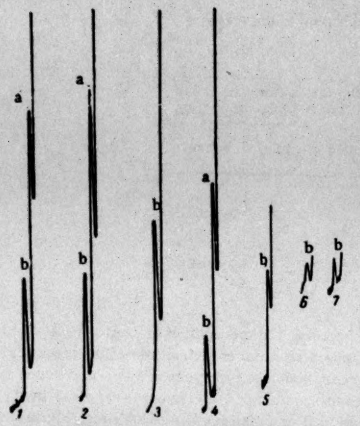

Fig. 4. Record of the Rb lines 780 and 794 mμ in the presence of potassium. 1, 2) KCl solution, 0.1 mg/ml + 5 μg Rb/ml; 3) KCl solution, 0.5 mg/ml + 5 μg Rb/ml; 4) KCl solution, 0.1 mg/ ml + 1 μg Rb/ml; 5) KCl solution, 10 mg/ml + 1 μg Rb/ml; 6) sample of sea water; 7) the same + 0.1 μg Rb/ml; a) peak for line Rb 780 mμ; b) peak for line Rb 794 mμ.

Determination of Rubidium in the Presence of Potassium. During determination of rubidium in natural materials (e.g.. in the ash from plants) difficulties may arise because of the proximity of the potassium lines 766.6-769.9 mμ to the rubidium line 794 mμ; it was of interest, accordingly, to establish the minimum amount of rubidium that can be determined, and the maximum permissible amount of potassium. The FÉU-22 was used and the spectrum was recorded in the region 775-803 mμ. As is evident from Fig. 4, in which are given some of the spectrum recordings, it was found possible to determine as little as 1 μg of Rb/ml in the presence of 10 mg KCl/ml; (0.01% Rb in KCl). At lower potassium contents it was possible to detect as little as 0.1 μg Rb/ml. Thus it was possible to determine Rb in a sample of sea water containing 0.04 μg Rb/ml after concentrating it by evaporating the sample four times; before carrying out the photometric measurements, 8 ml of the water which had been concentrated four times was diluted to 10 ml with water or with a solution of a rubidium salt to give an additional concentration of 0.1 or 0.2 μg Rb/ml (Fig. 4).

Determination of Calcium Present as an Impurity in Strontium Salts. During determination of calcium on the basis of its 422.7 mμ line in the presence of strontium salts, when ordinary photometric techniques are used, difficulties may arise as a result of the presence of the line of ionized strontium at 421.6 mμ [1]. The record of the spectrum on the recorder permits one in this case to readily evaluate the possible error arising from superposition of the strontium radiation. In Fig. 5 are shown records of the spectra of strontium nitrate solutions in the region 421-425 mμ without and with additions of 10 and 20 μg Ca/ml. The salt concentration of the solution was 20 mg/ml. The results of parallel determinations of calcium are close to each other, and calcium added to the solution (10 μg/ml) was determined with satisfactory accuracy.

TABLE 2

Determination of Calcium in a Solution of a Strontium Salt by the Method of Additions

Sample No.	Ca found in solution in parallel determinations, μg/ml				Mean value of Ca, g/ml	Ca added, μg/ml	Total content of Ca μg/ml	Ca. found in solution with additions μg/ml	Difference μg/ml
	1	2	3	4					
1	7,34	7,15	7,37	—	7,29	10	17,29	18,1	+0,8
2	8,06	8,65	8,32	8,18	8,30	10	18,3	17,9	—0,4

Determination of Calcium in Salts of the Rare Earths. In an acetylene-air flame the rare earths emit radiation, the complex molecular spectrum of which [7, 8] complicates the determination of calcium on the basis of the line 422.7 mμ. The use of a recording of the spectrum in the region 421-425 mμ makes it possible to determine the value of the photocurrent corresponding to the calcium radiation more accurately. The method was used for the analysis of yttrium and gadolinium salts (Fig. 6). Solutions containing 5-8 mg/ml of the salts (carbonates were dissolved in hydrochloric acid), and also solutions of the salts with the same concentration but containing additions of 1-3 μg of Ca/ml, were measured photometrically. The height of the peak corresponding to addition of

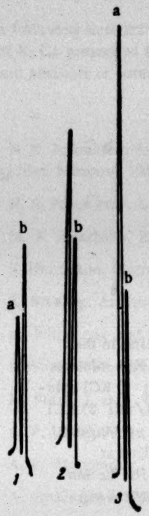

Fig. 5. Record of the Ca line 422.7 mμ in the presence of strontium. 1) 20 mg Sr/ml without addition of any Ca; 2) 20 mg Sr/ml + 10 μg Ca/ml; 3) 20 mg Sr/ml + 20 μg Ca/ml; a) peak of the line Ca 422.7 mμ; b) peak for the line Sr 421.6 mμ.

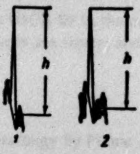

Fig. 6. Record of the Ca line at 422.7 mμ in the presence of yttrium and gadolinium. 1) Yttrium salt, sample No. 1, 5 mg/ml; 2) gadolinium salt, sample No. 2, 4 mg/ml.

1 μg Ca/ml amounted to about 15 divisions on the scale of the recorder tape, or 24 mm. Results of parallel determinations of calcium in some yttrium and gadolinium salts are given in Table 3.

Determination of Strontium in Sea Water. Determination of strontium in sea water is important from the viewpoint of the geochemistry of this element [9, 10]. The strontium concentration of water can amount to 8 μg/ml. A method has been published for the determination of strontium which is based on a combination of a radiochemical method and a flame photometric method [11], and also one based on direct flame photometry by the method of additions [12]. The other elements present in sea water in high concentrations which emit radiation in a flame, mainly sodium, magnesium, and calcium, make it essential that the flame background be determined accurately. The flame photometer in which the spectra are recorded makes it possible to carry out such a determination rapidly and accurately. Solutions of sea water which had been diluted twice, and the same diluted solutions to which 2, 4, and 8 μg Sr/ml had been added, were photometrically measured; the spectral region 549.0-459.0-465 mμ was recorded, and from the peak height the Sr content of the water was calculated, using the technique adopted for the work on the method of additions.

TABLE 3

Determination of Calcium in Yttrium and Gadolinium Salts by the Method of Additions

Sample	Ca added for the determinations μg/ml	Ca found in the salt, %	Deviation from the mean
Yttrium salt No. 1	1	0,0200	±0,0012
The same »	1	0,0224	
» No.2	1	0,0146	±0,004
» »	1	0,0154	
» No.3	1	0,00595	±0,00029
» »	1	0,00497	
Gadolinium salt No.1	1	0,0263	±0,0005
The same »	2	0,0252	
» No. 2	1	0,025	±0,002
» »	2	0,021	
» No. 3	1	0,035	±0,001
» »	2	0,037	

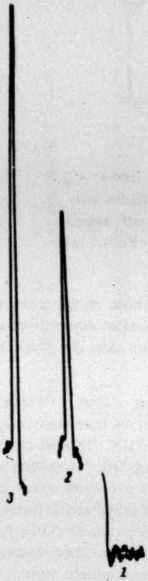

Fig. 7. Record of the Sr line 460.7 mμ in sea water. 1) Distilled water; 2) sea water diluted twice; 3) twice-diluted sea water + 2 μg Sr/ml.

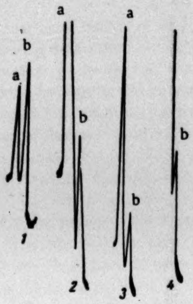

Fig. 8. Record of the Mn line in the presence of potassium. 1) KCl solution, 100 μg/ml + 5 μg Mn/ml; 2) KCl solution, 5 mg/ml + 5 μg Mn/ml; 3) KCl solution, 100 μg/ml, + 1 μg Mn/ml; a) peak for the potassium line at 404.4-404.7 mμ; b) peak for the Mn lines at 403.1, 403.3, and 403.4 mμ.

Fig. 7 is shown a record of the spectrum obtained on introducing into the flame distilled water which had been diluted twice with sea water, and the same water to which 2 μg Sr/ml had been added. The flame background arising from the introduction of sea water corresponds to a value equivalent to about 1 μg Sr/ml. In six parallel determinations the following values were found for the strontium content of the sea water: 6.8, 7.2, 6.84, 6.4, 6.92, and 6.92 μg Sr/ml, and average value of 6.84 μg/ml, the maximum deviation being ± 0.4 μg/ml, and the mean deviation 0.166 μg/ml, or 2.4% (relative).

Determination of Manganese in the Presence of Potassium. Manganese is determined on the basis of the lines of the resonance triplet with wavelengths of 403.1, 403.3, and 403.4 mμ; these are not separated in the spectrophotometers with low dispersion normally used. The proximity in the spectrum of the potassium lines 404.4 and 404.7 mμ, and the possible superposition of the potassium radiation on that of manganese, makes it essential to carry out an accurate control of the separation of the Mn and K lines; it is recommended that potassium be determined on the basis of the lines 766 6 and 769.9 and to apply a correction by means of a specially constructed curve [13] or by preliminary separation of potassium from manganese by precipitation in the form of manganese ammonium phosphate [14]. A record of the spectrum here again makes it possible to evaluate and take into account possible errors arising from the presence of potassium in solution. In order to establish the limiting permissible amounts of potassium and manganese, flame spectra were recorded in the region 402-405.5 mμ, for solutions containing various amounts of Mn and K salts. As is evident from Fig. 8 it is possible to determine as little as 1 μg Mn/ml of Mn in the presence of 10 mg KCl/ml. Correction for the background caused by superposition of the potassium radiation on an ordinary spectrophotometer in which the spectra are not recorded would be impossible in this case.

SUMMARY

The design of a recording flame spectrophotometer is described in which the spectrum is recorded on paper; the advantages of this apparatus over the usual type of spectrophotometer are demonstrated, taking as examples the determination of metals in the presence of other metals which give complex molecular spectra in the spectral region of the test line, or give lines which are close to this test line.

The following determinations are described: determination of Li in NaCl; Rb in the presence of predominant amounts of K; Ca present as an impurity in Sr salts and rare earth salts; Sr in sea water; and Mn in the presence of predominant amounts of potassium.

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POLAROGRAPHIC REDUCTION OF HALOGENATES AND THEIR OXIDATION POTENTIALS

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The value of the equilibrium potential of an oxidizing agent containing oxygen is known to be dependent on the acidity of the solution. Theoretically, this relation can be expressed by the formula:

$$E = E_0 + \frac{RT}{nF} \ln \frac{a_{\text{oxid.}} \cdot a_{\text{H}}}{a_{\text{red.}}}.$$

However, calculations based on this formula cannot be carried out in practice, since the activity values are not always known, while substitution of concentration for activity leads to values which do not agree with the values determined experimentally. As an example one may instance the work of Kolthoff and Luther [1], in which it was shown that the change in the potential of the system $Cr_2O_7^{2-}/Cr^{3+}$ arising from a unit pH change, not only did not agree with the calculated value, but differed in sulfuric and hydrochloric acid solutions.* In a number of papers, Syrokomskii, Avilov, et al. [3-7] also demonstrated disagreement between the oxidation–reduction potentials measured in various media and the theoretical and published values. In addition, published values of the potentials cannot characterize the reducibility of halogenates under the currents applied during polarography with a dropping-mercury electrode or with a platinum rotating electrode. Thus, according to published results [8], chlorate has the highest normal oxidation potential (in the halogen series), while iodate has the lowest; on the other hand, it is well known that chlorate is not reduced during electrolysis with a dropping-mercury cathode, and iodate and bromate are polarographed quantitatively, the half-wave potentials and the wave height being functions of the pH [9-14].

However, the work carried out already referred to a comparatively narrow acid concentration range, and, in in general, no work has been carried out in sulfuric acid. Accordingly, the work described here was devoted to establishing the effect of sulfuric acid concentration (from 2 to 32 N) on the polarographic reduction of halogenates.

Since hydrogen invariably participates during the electrical reduction of most oxygen-containing anions, the material from which the electrode is made should play an important part; accordingly, we polarographed the halogenates not only on a dropping-mercury electrode but also on a platinum electrode.

In order to compare the polarographic reduction potentials of the halogenates (i.e., potentials when current is applied) with the oxidation potentials, we measured the potentials in solutions of the halogenates with varying sulfuric acid concentrations in the absence of a current.

1. Polarography of the Halogenates with a Dropping-Mercury Cathode. Polarographic experiments were carried out on a PPT-1 visual polarograph made by the experimental shop of the Institute of Energetics, Academy of Sciences, Kazakh SSR. The M-21 type galvanometer had a sensitivity of 10^{-9} amp/mm/m. The half-wave potentials were determined graphically as the point of intersection of the straight line constructed within the

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*It was shown in Ptitsyn and Petrov's paper [2] that the potential of this system is completely independent of trivalent chromium ions.

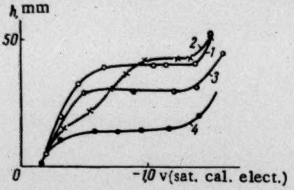

Fig. 1. Polarograms for 4 × 10^{-3} M chlorate solutions. Sulfuric acid concentration: 1) 18 N; 2) 22 N; 3) 24 N; 4) 32 N.

TABLE 1.

Characteristics of the Polarograms of Sulfuric Acid Solutions of Chlorate. Chlorate Concentration 4 · 10^{-3} $M^{2/3}$ $t^{1/6}$ = 2.4

Sulfuric acid concentration, N	I_d, μa	$I_d/m^{2/3}t^{1/6}$	$E_{1/2}$, V	n
16	20,0	8,3	—0,67	0,1
18	16,8	7,0	—0,59	0,1
20	14,0	5,8	—0,54	0,2
22	16,0	6,6	—0,39	0,3
24	12,0	5,0	—0,33	0,3
26	8,0	3,3	—0,39	0,3
28	6,8	2,8	—0,35	0,3
30	4,8	2,0	—0,25	0,3
32	6,4	2,7	—0,25	0,3
34	8,0	3,3	—0,25	0,3
36	8,0	3,3	—0,30	0,3

coordinates log $i/(i_d-i)$-E with the potential axis. The potential values given below are corrected for IR and refer to the saturated calomel electrode. Dissolved oxygen was removed by passing hydrogen or carbon dioxide through the solution prior to addition of the halogenate (0.1 ml).

a) Chlorate. Results obtained during the polarographic study of chlorate* are given in Fig. 1 and in Table 1. A reduction current was only observed on the polarograms when the sulfuric acid concentration was not less than 10 N. During oscillographic polarography, which is more sensitive, it was possible to observe reduction of chlorate at lower sulfuric acid concentrations [15]. A clearly defined wave was observed in 16 N and in higher concentrations of sulfuric acid when ordinary polarography was used.

The wave height is proportional to the chlorate concentration and depends on the sulfuric acid concentration, passing through a maximum at approximately 16 N sulfuric acid, and again increasing somewhat in 32 N acid. Such a relation is connected, probably, with the viscosity of the medium; starting at concentrations higher than 16 N, the viscosity of the sulfuric acid solutions increases, in the range 29-31 it changes to a small extent, while in the range 32-35 N there is again a certain drop in viscosity.

However, the effect of sulfuric acid concentration on the reduction process is also connected with chemical interactions between chlorate and sulfuric acid, in the course of which it is known [16] that chlorine dioxide, chlorous, and perchloric acids are formed, as well as free chlorine, all of which can be reduced on the cathode (with the exception of perchloric acid and its anions, which, according to published results [10, 11] and according to our results, do not give polarographic waves in the absence of special catalysts)

The most probable participants in the electrode process are chlorine dioxide and chlorine, the presence of which can be observed from the yellow-green color of the solution and from its odor. It should be pointed out that during polarographic investigation of a solution from which chlorine dioxide and chlorine had been removed by extraction with organic solvents or by heating, no reduction waves were observed.

Qualitative changes in the composition of the solution are reflected in changes in the values of the half-wave potentials (Table 1).

b) Bromate. Bromate is known to be reduced on the dropping-mercury cathode in weakly alkali and acid media of varying composition [9, 11, 12, 14]. We established that in a supporting electrolyte of 2 N sulfuric acid, bromate forms one very clearly defined reduction wave ($E_{1/2}$ - 0.4 volt). However, even in 4 N sulfuric acid, another wave appears which precedes the main bromate wave, and starting at 0 volt, it persists at higher acid concentrations (Fig. 2). We think that this wave is determined by the reduction of mercury ions formed as the result of the direct interaction of bromate with mercury metal. Exactly the same wave is also obtained in solutions of other oxidizing agents—dichromate, permanganate [17]—which oxidize metallic mercury.

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*The experiments were carried out by R. Sh. Nigmetova.

TABLE 2

Characteristics of the Polarograms of Sulfuric Acid Solutions of Iodate. Iodate Concentration 2.4 10^{-3} M; $m^{2/3} t^{1/6}$ - 1.7

Sulfuric acid concentration	I_d, μa	$I_d/m^{2/3} t^{1/6}$	$E_{1/2}$, v	n
First wave (reduction of mercury ions)				
2	No wave			
6	No wave			
8	3,6	2,1	+0,34	—
10	4,6	2,7	+0,36	—
14	4,1	2,4	+0,37	—
16	4,1	2,4	+0,30	—
18	4,6	2,7	+0,30	—
20	4,1	2,4	+0,25	—
Second wave (reduction of iodic acid molecules)				
2	13,3	7,8	—0,13	0,6
6	18,9	11,1	—0,03	—
8	15,3	9,0	—0,09	—
10	10,7	6,3	—0,08	—
14	6,1	3,6	—0,10	0,6
16	4,1	2,4	—0,10	—
18	2,6	1,5	—0,16	—
20	Wave poorly expressed			
Third wave (reduction of iodate anions)				
2	17,9	10,5	—0,69	0,6
6	25,1	14,8	—0,89	0,3
8	30,2	17,8	—0,95	0,3
10	28,2	16,6	—0,93	0,3
14	29,7	17,5	—0,99	0,3
16	2,6	1,5	—0,56	—
18	1,5	0,9	—0,56	—
20	No wave			

At acid concentrations of 6 N and higher, between the first (mercury) and second, main (bromate) wave, there is observed yet another wave which is not very clearly defined; this is the result, apparently, of the reduction of the bromic acid molecule [13, 14]. Since bromic acid is a fairly strong acid, the concentration of its undissociated molecules in equilibrium with its anions is relatively low, and the wave does not have a clearly defined shape; at higher sulfuric acid concentrations this "molecular" wave, in general, disappears.

The absence of clear lines of demarcation between the waves prevents one from calculating the polarographic characteristics. The height of the total wave depends on the acid concentration, and attains a maximum in approximately 10 N acid. The chemical interaction of bromate with acid is more clearly marked the higher the acid concentration; this chemical interaction gradually leads to a complete change in the composition of the solution, an idea of which can be gained from the external appearance of the solution, which acquires a rosy-orange or yellow color (extracted by chloroform or carbon tetrachloride), the latter is caused by the formation of free bromine, and possibly bromine dioxide. Under these conditions, the total wave height decreases sharply and disappears in approximately 22 N acid. When the acid concentration is increased further, this wave is replaced by another (curve 5, Fig. 2) located at a considerably more negative potential ($E_{1/2}$ = - 0.6 volt) than in less acid solutions (Curve 3, Fig. 2).

c) Iodate. Results of these experiments are given in Table 2 and Figs. 3 and 4. It is clear from these results that reduction of iodate in general proceeds in a way similar to that of bromate: depending on the acid concentration, waves for the reduction of mercury ions (Fig. 3, curve 3 step I), iodic acid (curves 1, 2, 3 step II), and of iodate (step III on the same curves) are observed. In these experiments the second step on the polarogram is expressed very clearly, since iodic acid dissociates to a very small extent. The limiting current in this case is observed at potentials close to the null discharge potential (-0.2 volt), i.e., under conditions which are most favorable for the reduction of uncharged particles.

The relation between the heights of the individual waves and the acid concentration, is, in general, similar to that described above for bromate. However, already in 18 N acid, there is observed an "infinite" current at a potential which is more positive than the reduction potential of hydrogen in the given supporting electrolyte (curves 1 and 2, Fig. 4); in this case the height of the other steps (as compared with curve 3, Fig. 4) decreases sharply, and in 30 N acid these steps disappear completely (curve 3, Fig. 4)—there remains only a sharp increase in the current at -0.6 volt. Since this potential is approximately 0.4 volt more positive than the hydrogen liberation potential (curve 1, Fig. 4), it remains to suggest that this wave appears as the result of some new electrode process, or, most probably, has a catalytic character. We should point out incidentally, that similar catalytic waves have been observed by Lingane [18] during reduction of perrhenate in various buffer solutions, and, later by us during the reduction of perrhenate in a sulfuric acid mediun [19].

As is evident from Tables 1 and 2, in which the number n calculated from the slope of the straight lines constructed within the coordinates $\log i/(i_d - i)$—E, is given, reduction of the halogenates is irreversible. This might have been expected since the anion being reduced suffers profound changes in composition.

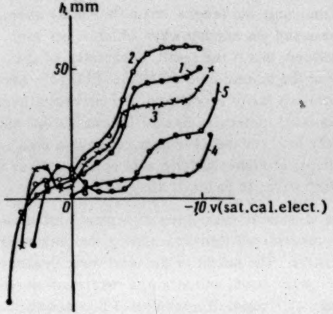

Fig. 2. Polarograms of 8 x 10^{-3} M iodate solution. Sulfuric acid concentration: 1) 6 N; 2) 10 N; 3) 14 N; 4) 22 N; 5) 26 N.

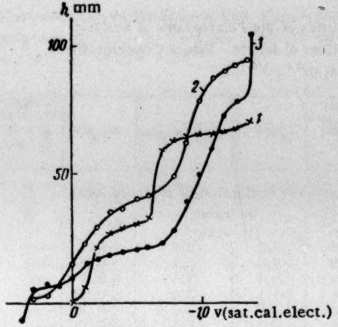

Fig. 3. Polarograms of 2 x 10^{-3} M iodate solution. Sulfuric acid concentration: 1) 2 N; 2) 6 N; 3) 14 N.

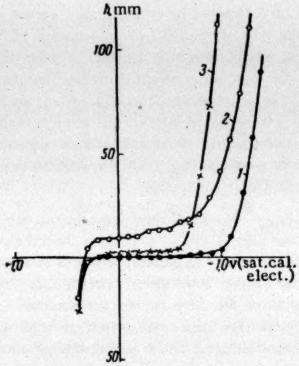

Fig. 4. Polarograms of 10^{-3} M iodate solution in a supporting electrolyte of concentrated sulfuric acid solutions: 1) 18 N sulfuric acid without iodate; 2) 18 N sulfuric acid; 3) 30 N sulfuric acid.

Comparison of the results obtained during polarographic studies of chlorate, bromate, and iodate, shows that the reducibility of these ions increases from chlorate to bromate and iodate.

The presence of several waves on the polarograms of iodate and bromate confirms the qualitative changes which occur in solution under the influence of sulfuric acid, while the inconstancy of the half-wave potential within the limits of these separate waves testifies to the instability of the systems formed, and to their simultaneous coexistence in the test solution.

Results of potential measurements in the absence of a current also point to these qualitative changes which are connected with the appearance of new forms which are distinguished by higher oxidation potentials.

2. Measurement of Potential in the Absence of Current. The potentials were measured on a PPTV-1 potentiometer. • The indicator electrode was a smooth platinum wire. The reference electrode was a saturated calomel electrode. The temperature of the solution was 25 ± 1°. Measurements are carried out 5 minutes after addition of the halogenate to the acid solution.

It should be pointed out that the experimental determination of the potentials of the systems halogenate–halide are impossible in actual fact, since halide ions in an acid medium are oxidized by halogenate with formation of a free halogen (the values given in textbooks are obviously calculated on the basis of Luther's law from the potential values of the systems halogenate–halide and halogen–halide). Accordingly, in our experiments, the solutions only contained halogenate (4 x 10^{-3} M) and from 2 to 36 N sulfuric acid.

Results of these measurements are given in Fig. 5. When the values which we obtained in 2 N sulfuric acid are compared with the values of the normal potentials (as is well-known, the values of the normal potentials of

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• V. P. Gladyshev took part in this work.

the oxidizing agent correspond usually to 2 N sulfuric acid), what is immediately striking is the directly contradictory way in which the potentials change, namely

	Chlorate	Bromate	Iodate
The potential which we measured in a 10^{-3} solution of halogenate in 2 N sulfuric acid	± 0.39	+ 0.41	+ 1.12
The normal potential of the halogenate system (free halogen according to Latimer [20])	+ 1.47	+ 1.52	+ 1.20
The normal potential of the system halogenate–halide ions [8]	+ 1.44	+ 1.42	+ 1.08

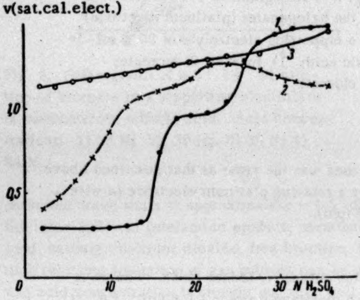

Fig. 5. Relation between the potential of 10^{-3} M solutions of the halogenates (in the absence of a current) and the sulfuric acid concentration: 1) chlorate; 2) bromate; 3) iodate.

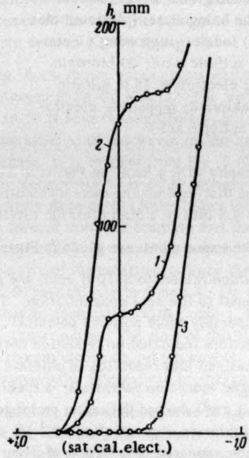

Fig. 6. Polarograms of a 10^{-4} M solution of iodate in a supporting electrolyte of sulfuric acid (platinum electrode). Sulfuric acid concentration: 1) 2 N; 2) 4 N; 3) supporting electrolyte, the curves coincide for all acid concentrations.

Thus, in 2 N sulfuric acid, iodate is the stronger oxidizing agent. This fact is in good agreement both with the results given above of our experiments, and with the observations and calculations of Sammet [21], who found that the equilibrium constant, on switching from halogen decreases from chlorate to iodate, and that consequently, the oxidizing capacity of iodate is higher than that of the other halogenates.

With increasing sulfuric acid concentration, the potential of the iodate increases uniformly, while the potential of the chlorate increases stepwise, indicating sudden changes in the composition of the solution. Bromate occupies an intermediate position between iodate and chlorate (Curve 2, Fig. 5). The slight drop which occurs at high sulfuric acid concentrations should presumably be related to the limited solubility of bromine in concentrated sulfuric acid. Where this is not the case, then, in all probability, at high acid concentrations, the curve for bromate would be located at approximately the same potentials as for the chlorate curve, and would intersect the iodate curve just like the chlorate curve does. Or, putting it in another way, the published order of the sequence of the potentials according to their potentials (chlorate, bromate, and iodate) could be achieved in real conditions when the sulfuric acid concentration exceeds 27 N (Fig. 5).

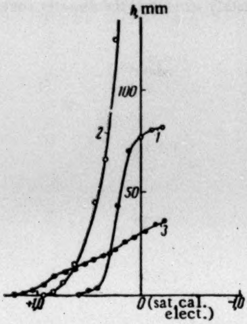

Fig. 7. Polarograms of 10^{-3} M solutions of the halogenates (platinum electrode). 1) Iodate; supporting electrolyte 16 N sulfuric acid; 2) bromate, supporting electrolyte 16 N sulfuric acid; 3) chlorate; supporting electrolyte 22 N sulfuric acid.

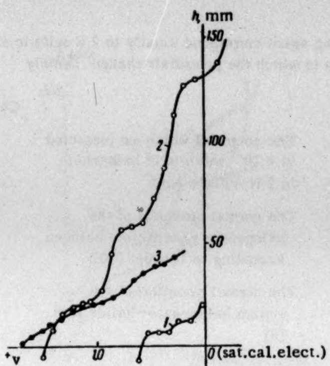

Fig. 8. Polarograms of 10^{-3} M solutions of the halogenates (platinum electrode) in a supporting electrolyte of 30 N sulfuric acid; 1) Iodate; 2) bromate; 3) chlorate.

3. Polarography with a Rotating Platinum Electrode. The setup used was the same as that described above, with the exception that the dropping-mercury electrode was replaced by a rotating platinum electrode (a wire ~ ~ 3 mm long and 0.5 mm in a diameter; the rotational rate was ~ 400 rpm).

Results of the experiments are given in Figs. 6-9.

In Fig. 6, which relates to 2-10 N acid, are given typical reduction curves for iodate alone. The wave height is proportional to the acid concentration. The potential at which the wave starts is + 0.6 volt., i.e., it appears at a considerably more positive potential (by almost 0.6 volt) than on a dropping-mercury electrode. At the acid concentrations indicated, no reduction curves were observed on the polarograms for chlorate and iodate. It should be emphasized that reduction of chlorate on a platinum electrode generally does not occur in practice, even at the hydrogen reduction potentials: a specially conducted "macro test" (current density 0.2 amp/cm^2, electrode surface 1 cm^2) showed that after prolonged electrolysis (more than 2 hours) of a solution of chlorate in 2 N sulfuric acid (chlorate concentration 10^{-2} M) which was accompanied by intense liberation of hydrogen, only a slight opalescence appeared on addition of silver nitrate. When the same experiment was repeated with a mercury electrode, the chlorate was reduced almost completely in a matter of minutes.

At acid concentrations ranging from 12 to 22 N (Fig. 7), reduction currents are observed for all three halogenates. Iodate gives a wave similar to that described above, but its height is lower, presumably, as a result of an increase in the viscosity of the sulfuric acid solution. The reduction potential does not change with increasing acid concentration—this indicates that either the same products that were reduced at lower acid concentrations are reduced at the cathode, or that the new materials formed in the solution are reduced at the same potential as the iodate itself. Actually, on taking polarograms of a solution containing known amounts of iodate and free iodine simultaneously, we again observed only one wave which coincided in potential with the wave obtained when no free iodine had been added.

It should also be pointed out that the final product of the electrode reduction of iodate—iodide ions cannot exist in acid solutions at the same time as iodate, since it reacts with the latter according to the equation 10 $IO_3^- + I^- + 6H^+ \rightarrow I_2 + 3H_2O$.

Free iodine, as is well-known, is readily reduced on a platinum electrode, and the reduction product (iodide) is again oxidized by iodate according to the equation just given. Thus, apparently, only free iodine is subjected to electrode reduction, while reduction of the iodate proceeds mainly as the result of a chemical reaction in solution.

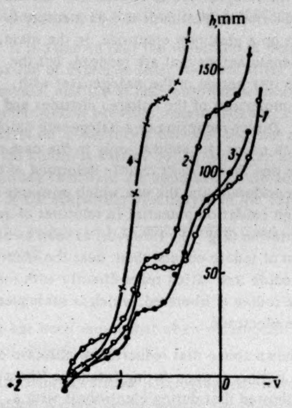

Fig. 9. Polarograms of a 8 · 10^{-4} M solution of bromate in a supporting electrolyte of concentrated sulfuric acid. Acid concentrations: 1) 28 N; 2) 30 N; 3) 32 N; 4) 34 N.

In bromate solutions, in a supporting electrolyte of 12-22 N acid, the reduction currents appear at a potential of about + 1.2 volt, and the current increases so strongly that the galvanometer needle goes off the scale (even when the galvanometer is shunted to its limit). Apparently, reduction of the products formed by the interaction of bromate and sulfuric acid occurs, while the sharp increase in the current is catalytic in character.

In chlorate solutions the reduction currents only appear at acid concentrations of ~ 16 N. The potential at which reduction starts is strongly dependent on the acid concentration, and shifts to more positive values with increasing acid concentration. This is readily explained by the fact that with increasing acid concentration, the amount of the products formed by the interaction of the acid and chlorate increases. The fact that the reduction processes occur at the same time leads to a wave which is not clearly defined (Curve 3, Fig. 7).

In Fig. 8 are shown polarograms which are typical of those obtained in 24-36 N acid. The wave height of the iodate in 30 N acid is insignificant, but its potential is almost the same as of the waves in less concentrated acids. Bromate, as is evident from Fig. 8 (Curve 2) gives very clearly defined waves in 30 N sulfuric acid; the reduction wave starts at approximately + 1.5 volt. The presence of three steps on the wave indicates reduction of the three different interaction products mentioned above, which are formed from the bromate and the concentrated acid, namely—bromine dioxide, free bromine, and, possibly, free oxygen [20]. It should be pointed out that in such solutions liberation of gas bubbles can be observed. The complexity of the relation between the wave height and acid concentration is brought out very well in the curves in Fig. 9, particularly by Curve 4. On this curve the first step (starting from positive potential values) dropped considerably in comparison with Curve 1, the second step increased by four times, while the last step went off the galvanometer scale. The start of this step occurs at a potential approximating to that for reduction of oxygen on a platinum electrode, which enables one to suggest that the wave is connected with the reduction of oxygen, and, apparently, is catalytic in character.

The results described which were obtained on taking polarograms on a platinum electrode agree very well with the way in which the potentials of the halogenates change with the sulfuric acid concentration in the absence of a current (Fig. 5). The iodate potential which is relatively high already in 2 N sulfuric acid: + 0.87 volt. (+ 1.12 volt relative to the saturated calomel electrode) does not undergo any sharp changes as the sulfuric acid concentration increases; in agreement with this, when solutions of iodate are polarographed with a platinum electrode in a supporting electrolyte of acid, only one wave is observed whatever the acid concentration.

The potentials of chlorate and bromate change very rapidly with increasing acid concentration, and the polarographic behavior of these anions on a platinum electrode changes accordingly. Thus, the potential of the chlorate remains almost constant and very low—about + 0.05 volt (+ 0.3 volt with respect to the saturated calomel electrode) right up to sulfuric acid concentrations of the order of 14 N, after which it sharply increases up to + 0.7 volt (+ 0.95 volt with respect to the saturated calomel electrode). It is precisely at the acid concentration indicated that the reduction current appears on the platinum electrode, starting at a potential of about + 1.05 (+ 1.3 volt with respect to the saturated calomel electrode). The appearance of the second step on the polarogram, when the latter is taken in a supporting electrolyte of concentrated acid (higher than 22 N), is in good agreement with the second increase in the potential in the absence of a current, which is observed at this acid concentration.

The Mechanism of the Polarographic Reduction of the Halogenate. Comparison of the experimental results obtained with the platinum and mercury electrodes draws attention to the fact that reduction on platinum occurs at considerably higher positive potentials than on mercury. Under such conditions the reduction wave is located at

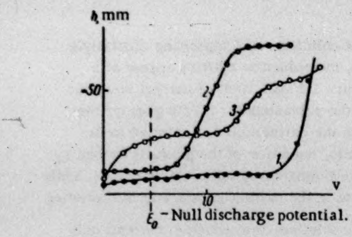

Fig. 10. Polarograms of a 10^{-4} M solution of iodate in a supporting electrolyte of dilute (10^{-3} M) solutions of sodium sulfate and sulfuric acid: 1) Sodium sulfate solution; 2) iodate in a supporting electrolyte of sodium sulfate; 3) iodate in a supporting electrolyte of sulfuric acid.

potentials where reduction of hydrogen does not yet occur. This fact compels one to assume that the mechanism of reduction on platinum and on mercury is different, thus: on a platinum electrode, in the main, it is not halogenate anions that are reduced, but the products of the interaction of the halogenates with sulfuric acid—molecules of the halogen dioxides and free halogens. Direct reduction of a halogenate anion on platinum can occur, apparently, only in the case of the iodate, the one that is most readily deformed of the three anions considered, and the one which possesses a sufficiently high oxidation potential in solutions of acids of any concentration (Fig. 5). However, as soon as electrode reduction of iodate occurs, then, near the electrodes there appear iodide ions which react directly with iodate; as a result free iodine is liberated, which is subsequently reduced on the electrode.

It was shown above that reduction of chlorate on platinum does not occur even during intensive liberation of hydrogen. Similar experiments with bromate and iodate solutions * showed that during electrolysis with a platinum electrode, in iodate solutions, immediately after switching on the current, there is observed liberation of free iodine; while in solutions of bromate, free bromine only appears several minutes after the beginning of electrolysis.

Reduction of all three halogenates occurs on a dropping mercury electrode, iodate and bromate give well defined polarographic waves; chlorate ions, which are the most electronegative as compared with bromate and iodate, do not give waves because of the overwhelming liberation of hydrogen (the wave which appears in ~ 16 N acid is caused by the reduction, not of chlorate as such, but of chlorine dioxide).

One cannot but notice that in their behavior during electrolysis the halogenates are similar to polar organic compounds, which, as is known [22], can only be electrolytically reduced on cathodes made of metals with a high overvoltage for liberation of hydrogen, in particular, on mercury.

The mechanism of the reduction of oxygen-containing anions of the halogenate type on a mercury cathode, apparently, differs essentially from the reduction mechanism of the readily reducible anions studied by A. N. Frumkin et al. In the work of Kryukova [23], Frumkin and Florianovich [24, 25], and in other articles of the Frumkin school [26, 27] it has been shown that during the polarographic reduction of persulfate, chloroplatinate, chloroiridiate, and some other anions, a minimum current is observed on the polarization curve in a potential region which is more negative than the potential of the mercury zero discharge. The current drop can be eliminated by adding excess of an indifferent electrolyte. The authors of the articles cited above explain these phenomena by the fact that the electrostatic repulsion of the anion from the negatively charged surface of the cathode leads to a drop in the concentration of the anion near the cathode. Cations which enter into the composition of a double salt on addition of an excess of an indifferent electrolyte facilitate the approach of the anions to the cathode.

However, during reduction of such anions as MnO_4^- and HgI_4^{2-}, Florianovich and Frumkin [25] did not observe current minima. This phenomena has not been explained in the articles cited above. In our opinion the most likely reason for such "anomalous" behavior on the part of anions of the type MnO_4^-, is that these anions oxidize the mercury of the electrode, and the wave which is observed when polarograms are taken of solutions of these oxidizing agents is determined by the reduction of mercury ions formed as the results of the chemical reaction of the latter with the solution. It should be noted that Kolthoff and Orlemann [14] when working with iodates and bromates pointed out the necessity of removing the mercury pool from the electrolyzer in order to avoid accumulations of mercury ions in solution. We have pointed out the fact that permanganate oxidizes mercury during polarographing earlier [17]. Kivalo and Laitinen hold the same view with respect to chloroplatinate [28]. As for the complex anion HgI_4^{2-}, which was mentioned above, it too is an oxidizing agent as far as mercury metal is concerned.

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* K. Sagadieva took part on this work.

In order to compare our results with those obtained by the Frumkin School, we carried out a series of experiments in which iodate solutions were polarographed in the absence of excess of an indifferent electrolyte. As is evident from the curves in Fig. 10, no current minima were observed at potentials more negative than the mercury zero discharge potential either in neutral (Curve 2) or in weakly acid solutions (Curve 3).

If it is assumed that the reduction of persulfate according to the scheme $S_2O_8^{2-} + 2e \rightarrow 2\ SO_4^{2-}$, i.e., without participation of hydrogen ions, does not differ in principle from the reduction of the oxygen-containing anions which we examined, and which only proceeds with the participation of hydrogen ions, then the absence of current minima on the polarograms becomes understandable; it is explained by the fact that during the electrical reduction of the halogenates on a mercury electrode, the first act of the electrode process is the discharge of hydrogen ions. Reduction of the anions is carried out by hydrogen at the moment of its formation. The hydrogen ions in the layers near the electrode facilitate the approach of the anions to the cathode, playing, in this way, a part similar to that of the cations of the supporting electrolyte in the experiments of Frumkin, et al.

The authors wish to express their thanks to M. T. Kozlovskii for his valuable advice and help in carrying out this work.

SUMMARY

It has been shown that when polarograms are taken with a dropping mercury electrode in a supporting electrolyte of sulfuric acid:

a) chlorates are not polarographed directly; in concentrated sulfuric acid solutions (not less than 16 N) it is the products formed by the interaction of chlorate with sulfuric acid that are polarographed;

b) bromates and iodates are polarographed even in dilute sulfuric acid, and in the case of bromates one clearly defined wave is observed, while in the case of iodates two clearly defined waves are observed.

It has been shown that bromate and iodate oxidize the mercury of the electrode, as a result of which a wave for the reduction of mercury ions appears on the polarograms.

It has been shown that, in the main, it is not the halogenates which are subjected to reduction on a platinum electrode, but the products of their interaction with sulfuric acid.

It has been shown that there is a complex relation between the wave height and the sulfuric acid concentration, as a result of simultaneous changes in the composition of the solution and in its viscosity.

The potentials of the halogenates in sulfuric acid of various concentrations have been measured in the absence of a current, and a relation has been established between the value of these potentials and the reducibility of the halogenates on dropping mercury and platinum cathodes.

On the basis of the experimental results obtained, some observations are made regarding the mechanism of the reduction of the halogenates.

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THE USE OF THIOSEMICARBAZIDES IN ANALYSIS

COMMUNICATION 3. TITRIMETRIC DETERMINATION OF THIOSEMICARBAZIDES WITH MERCURIC NITRATE*

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It was shown earlier [1] that thiosemicarbazides form complex compounds with cupric ions—copper thiosemicarbazidinates. Aryl- and diarylthiosemicarbazides are particularly sensitive reagents for cupric ions. The copper diarylthiosemicarbazidinate formed, on dissolving in water, acetic acid, alcohols, and some other organic solvents, colors the solution (if dilute) an intense blue or blue-green. The reaction of thiosemicarbazides with cupric ions is at the same time a highly selective reaction for the qualitative detection and quantitative determination of copper by a photometric method.

By the action of uni- and divalent mercury ions and of silver ions on copper thiosemicarbazidinate, substitution of the copper ions in its thiosemicarbazidinates by mercury or silver ions occurs, with simultaneous change in the blue or blue-green color of the solutions to a colorless or pale-yellow color. This characteristic of the reaction has served as a basis for using it for the quantitative determination of mercury [2].

In the present article a description is given of a titrimetric method for the quantitative determination of thiosemicarbazide, 1-phenyl-, 1,4-diphenyl-, 1-phenyl-4-ortho-tolyl-, and 1-phenyl-4-ortho-anisylthio-semicarbazides based on their capacity to form stable complex compounds with divalent mercury ions. The indicator in these titrations is copper thiosemicarbazidinate—$[Cu(RHNNHCSNHR)]^{2+}$, which is formed by adding a solution of cupric nitrate to the test solution of the thiosemicarbazides.

During titration, in all cases, two volumes of a 0.02 M solution of thiosemicarbazide, aryl-, or diarylthiosemicarbazide are expended for one volume of 0.02 M cupric nitrate solution (Table 1).

Thiosemicarbazide and its aryl- and diaryl derivatives react with mercuric nitrate according to the equation

$$Hg^{2+} + 2RHNNHCSNHR_1 \longrightarrow [Hg(RHNNHCSNHR_1)]^{2+}$$

The molecular weight and the structure of the thiosemicarbazides do not affect the number of the molecules of the thiosemicarbazide which are coordinated by the mercury ion.

1-Phenylthiosemicarbazide was also determined by means of a 2% alcoholic solution of diphenylcarbazone, which is widely used as an indicator in mercurometry.

The results obtained during the determination of 1-phenyl-thiosemicarbazide at pH 1.5-2 in the presence of diphenylcarbazone and cupric ions were in good agreement with each other. One of the drawbacks of diphenylcarbazone as an indicator is the necessity of maintaining a definite acidity for the solution. When the product formed by the reaction of mercury ions and the test material is precipitated, or forms a turbidity, it is difficult

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*For communication 2, see [1].

TABLE 1

Ratio of the Volumes of Solution Used during Titration of 0.02 M Solutions of the Thiosemicarbazides with $Hg(NO_3)_2$ in the Presence of $Cu(NO_3)_2$

Thiosemicarbazide	Amt. of 0.02 M thiosemicarbazide solution taken, ml	Amount of 0.02 M $Hg(NO_3)_2$ solution used ml	Molar ratio
Thiosemicarbazide - $H_2NNHCSNH_2$	25,0 20,0 10,0	12,60 10,04 5,1	1,98 1,99 1,96
1-Phenylthiosemicarbazide $C_6H_5NHNHCSNH_2$ –	30,0 20,0 10,0	15,05 10,1 5,05	1,99 1,98 1,98
1,4-Diphenylthiosemicarbazide $C_6H_5NHNHCSNHC_6H_5$ –	25,0 14,5 10,0	12,5 7,25 5,01	2,00 2,00 1,99
1-Phenyl-4-ortho-tolylthiosemicarbazide $C_6H_5NHNHCSNHC_6H_4CH_3$ –	25,0 20,0 15,0	12,5 10,05 7,45	2,00 1,99 2,01
1-Phenyl-4-ortho-anisylthiosemicarbazide $C_6H_5NHNHCSNHC_6H_4OCH_3$ –	20,0 15,0 10,0	10,05 7,40 5,05	1,99 2,02 1,98

to detect the point at which the color changes near the equivalence point. In general, determination with diphenylcarbanzone in an acetic acid solution is impossible. The composition of the compound which diphenylcarbazone forms with mercuric ions is not known [3-4]. The method recommended for the quantitative determination of thiosemicarbazides is fairly accurate, is characterized by high selectivity, and is simple to carry out. Changes in the acidity of the medium do not have an appreciable effect on the experimental results.

A characteristic property of copper aryl- and diarylthiosemicarbazidinates is their ready solubility in isoamyl alcohol. In the presence of a small excess of cupric nitrate, aryl- and diarylthiosemicarbazides can be quantitatively separated by extraction from compounds which are insoluble in isoamyl alcohol. In contrast to copper aryl- and diarylthiosemicarbazidinates copper hiosemicarbazidinate is insoluble in isoamyl alcohol. The method of extracting with isoamyl alcohol is particularly convenient for the quantitative determination of aryl- and diarylthiosemicarbazides in dilute solutions, since they can then be concentrated in a small volume of solution.

Thiosemicarbazides are readily prepared in a chemically pure form, accordingly, they are used as original materials for standardizing the working solution of mercuric nitrate.

EXPERIMENTAL

The working solution of mercuric nitrate was prepared by dissolving chemically pure mercuric oxide or metallic mercury in nitric acid. Nitrogen oxides strongly interfere with the determination of thiosemicarbazides, accordingly, the former should be removed beforehand when the working solution is prepared from metallic mercury.

The working solution of mercuric nitrate was standardized against an aliquot of the same thiosemicarbazide which we intended to determine. Mercuric nitrate solutions can be kept for a long time without any appreciable changes in concentration.

Thiosemicarbazide was prepared from monohydrazine sulfate and potassium thiocyanate by evaporating a solution which had been neutralized with potassium carbonate to a syrupy state [5]. 1-Phenylthiosemicarbazide was synthesized by heating an acetic acid or aqueous solution of phenylhydrazine hydrochloride with potassium or ammonium thiocyanate [2, 6]. 1,4-diphenyl-, 1-phenyl-4-ortho-tolyl-, and 1-phenyl-4-ortho-anisylthiosemicarbazides were prepared from the corresponding isothiocyanates and phenylhydrazine by the reaction

$$C_6H_5NHNH_2 + SCNAr \rightarrow C_6H_5NHNHCSNHAr$$

TABLE 2

Determination of Thiosemicarbazide By Means of a $Hg(NO_3)_2$ Solution. Indicator C[illegible]$(NO_3)_2$

$H_2NNHCSNH_2$ taken, mg	CH_3COOH added, ml	$H_2NNHCSNH_2$ found, mg	Difference, mg
36,45	10	36,30	—0,15
36,45	20	36,32	—0,13
18,45	10	18,35	—0,10
45,55	10	45,65	+0,10
91,13	25	91,20	+0,07

TABLE 3

Determination of Aryl- and Diarylthiosemicarbazides with $Hg(NO_3)_2$ Solution. Indicator $Cu(NO_3)_2$

Thiosemicarbazide	Taken, mg	Found, mg	Difference, mg
1-Phenylthiosemicarbazide $C_6H_5(NH)_2CSNH_2$–	41,80	41,45	—0,35
	25,08	24,85	—0,23
	20,90	20,70	—0,20
	20,90	20,70	—0,20
1-Diphenylthiosemicarbazide $C_6H_5(NH)_2CSNHC_6H_5$–	48,60	48,50	—0,10
	48,60	48,52	—0,08
	87,60	87,25	—0,35
	87,62	87,35	—0,25
1-Phenyl-4-ortho-tolylthiosemicarbazide $C_6H_5(NH)_2CSNHC_6H_4CH_3$–	51,46	51,44	—0,02
	51,46	51,38	—0,08
	102,9	102,8	—0,1
	102,92	102,70	—0,22
1-Phenyl-4-ortho-anisylthiosemicarbazide $C_6H_5(NH)_2CSNHC_6H_4OCH_3$–	27,33	27,39	+0,06
	27,33	27,40	+0,07
	54,66	54,60	—0,04
	54,66	54,58	—0,08

Determination of Thiosemicarbazide. An approximately 0.02 M solution of thiosemicarbazide was prepared by dissolving an aliquot of the material in water with heating. To an accurately measured volume of the thiosemicarbazide solution was added an equal volume of concentrated acetic acid and 10-15 drops of 0.05 M cupric nitrate and the solution titrated with 0.05 M mercuric nitrate until the blue color of the solution vanished and the solution became colorless. Acetic acid was added in order to dissolve any precipitate which might be formed in a neutral solution.

When diphenylcarbazone was used as the indicator, titration was carried out without addition of acetic acid. To the aqueous test solution of the thiosemicarbazide was added 10-15 drops of a 2% alcoholic solution of diphenylcarbazone, and the solution titrated with mercuric nitrate solution until the solution acquired a violet color. A serious drawback in these titrations is the appearance at the end point of a turbidity which can lead to over-titration.

During determination of thiosemicarbazide with mercuric nitrate solutions of varying concentrations, it was established that the best and most consistent results are obtained when 0.05 M mercuric nitrate solution is used. When less concentrated mercuric nitrate solutions are used, the color of the solution at the end point is not so clear-cut and it is more difficult to establish the end point.

The results obtained are presented in Table 2.

Determination of Aryl- and Diarylthiosemicarbazides. The quantitative determination of aryl- and diarylthiosemicarbazides was carried out under the same conditions as those used for the determination of thiosemicarbazide, the only difference being that 1-phenylthiosemicarbazide was dissolved in 70-80% acetic acid, and the diarylthiosemicarbazides were dissolved in 90-98% acetic acid.

During titration of 1-phenylthiosemicarbazide, 1, 4-diphenylthiosemicarbazide and 1-phenyl-4-orthotolylthiosemicarbazide, and blue or blue-green color of the solution changed to yellow, while during titration of 1-phenyl-4-anisylthiosemicarbazide the color changed to orange. In order to avoid over-titrating, the last ml of mercuric nitrate solution should be added slowly over an interval of several seconds with careful stirring. 1-2 drops of indicator (0.05 M cupric nitrate) should be taken for 10-20 ml of the acetic acid solution of aryl- and diarylthiosemicarbazides being titrated. Large amounts of cupric nitrate render establishment of the point at which the color of the solution changes difficult.

The working solutions of mercuric nitrate used for determination of aryl- and diarylthiosemicarbazides may have a molarity of 0.05-0.02 M.

The experimental results are given in Table 3.

Determination of 1-phenylthiosemicarbazide in the presence of diphenylcarbazone as indicator was carried out under the following conditions. A 0.01-0.005 M solution of 1-phenylthiosemicarbazide was prepared by dissolving an aliquot of the preparation in a 20-25% aqueous alcohol mixture on heating. To 20-25 ml of the test solution was added 10-15 drops of a 2% alcoholic solution of diphenylcarbazone and the solution titrated with mercuric nitrate until a violet color was obtained. During the determination of 41.75, 33.40, 41.75, 20.9, and 20.9 mg of 1-phenylthiosemicarbazide the following amounts were found: 41.85, 33.30, 41.90, 21.00, and 21.00 mg.

SUMMARY

Conditions have been established for the quantitative determination of thiosemicarbazide, aryl-, and diarylthiosemicarbazides by titration with mercuric nitrate in the presence of cupric salts as an indicator.

It has been demonstrated that 1-phenylthiosemicarbazide can be titrated with a mercuric nitrate solution using diphenylcarbazone as indicator.

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TITRATION IN NONAQUEOUS MEDIA

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The physicochemical principles of titration in nonaqueous media have been the subject of study since the twenties of the present century [1-11]. In the period 1922-1946 not more than 50 papers were published on the practical application of titration in nonaqueous media; these have been devoted in the main to weak acids and bases [12-17]. Rapid development of the application of these methods in analytical chemistry only really started after 1947 [18-42].* Kolthoff [43] at the Analytical Section of the Union of Pure and Applied Chemistry delivered a paper on the theoretical principles of titration in anhydrous acetic acid, and emphasized that processes in nonaqueous media should attract the attention of chemists in general more and more, particularly that of analytical chemists.

Most of the analytical work carried out in the field of nonaqueous titration has been concerned with neutralization reactions, and reactions of acids and bases, on the strength of which it is possible, according to Brönsted's theory [4, 5, 6] to modify the solvent within fairly wide limits.

Neutralization Reactions

We have used potentiometric titration in nonaqueous media since 1953 as one of the methods for analyzing organic mixtures when the color change of the indicator is not clear. We used as reference electrode [44] a silver chloride electrode in a 5% solution of lithium chloride in anhydrous methanol for titration with potassium or sodium methylate solution, and the same electrode in a saturated solution of potassium chloride in glacial acetic acid for titration with a solution of perchloric acid in glacial acetic acid. We have used glass, antimony, molybdenum, tantalum, and other electrodes as indicator electrodes. In addition, in many cases, titration can be carried out with two indicator electrodes [45]; the best are glass and platinum electrodes. The same electrodes can be used for titrating in glacial acetic acid. It should be pointed out that the glass, platinum, and, above all, the antimony electrodes are very sensitive to contamination of the solution, which is very often found in organic products. The electrode is sometimes completely deactivated and titration becomes impossible. In general it is advisable to clean the electrodes carefully after titration.

Determination of Bases and Acids in Neutral Oils. Using the electrodes indicated, we have developed [46, 47] methods for the determination of phenols and acids, and also ammonia and natural bases in neutral fractions from coal tar. Separate determination of tenths and hundredths of a percent of ammonia and natural bases [46] is carried out in glacial acetic acid by titration with 0.1 N perchloric acid in glacial acetic acid. Under these conditions, ammonia gives the first potential jump, while the natural bases give the second jump.

Determination of phenols and acid in such oils can only be carried out in a dimethylformamide solution. Titration of solutions in aniline, pyridine, and other organic bases was tested but did not give good results.

Analysis of Technical Guanidine Nitrate. Modecka and myself [48] have developed a method for the determination of guanidine nitrate in the technical material which also contains ammonium nitrate and dicyandiamide.

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*For a bibliography on analytical work on titration in nonaqueous media see J. Minczewski and Z. Lada, Miareczkowanie potencjometryczne PWN, Warsaw, 1957).

Titration of the 8-Hydroxyquinolates of Copper, Vanadium, Uranium, and Molybdenum Extracted with Chloroform. The Extracts were Titrated with a Solution of Divalent Chromium Acetate in Dioxane

Metal		Taken, mg		Concentration of the $Cr(CH_3COO)_2$ Solution, N	Amount of $Cr(CH_3COO)_2$ solution used, ml		Metal found, mg		Relative error, %	
I	II	I	II		I	II	I	II	I	II
V		0,54	+	0,015	0,72	—	0,55	—	+1,8	—
		0,54	—	0,015	0,70	—	0,53	—	—1,8	—
		0,54	—	0,015	0,70	—	0,53	—	—1,8	—
		0,54	—	0,015	0,71	—	0,54	—	0,0	—
	Cu	—	1,00	0,021	—	0,76	—	1,00		±0,0
		—	2,00	0,021	—	1,50	—	1,98		—1,0
		—	2,00	0,021	—	1,54	—	2,03		+1,5
V	Cu	0,25	1,00	0,016	0,28	0,98	0,23	0,99	—8,0	—1,0
		0,21	0,50	0,016	0,29	0,46	0,20	0,47	—5,0	—6,0
		0,21	0,50	0,016	0,28	0,48	0,22	0,49	+5,0	—2,0
	U		2,50					2,44		—2,4
			2,50					2,49		—0,4
			2,50					2,57		+2,8
V	U	0,50	2,50				0,51	2,49	+2,0	—0,4
		0,50	1,00				0,51	0,99	+2,0	—0,0
		0,50	2,00				0,49	2,06	—2,0	+3,0
	Mo		1,00					0,99		—1,0
			1,00					0,98		—2,0
			1,00					1,04		+4,0
		0,20	1,00				0,20	0,98	± 0	—2,0
V	Mo	0,20	1,00				0,18	0,96	—10,0	—4,0
		0,20	1,00				0,22	1,05	+10,0	+5,0

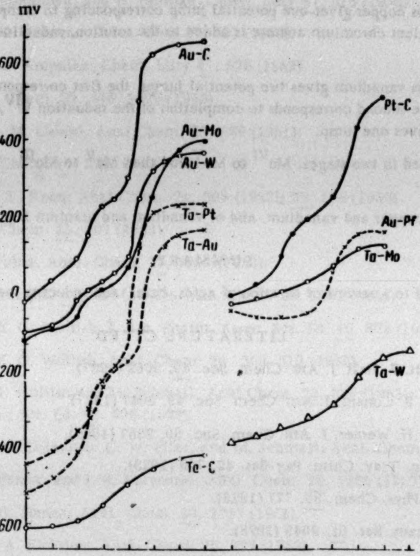
Total ammonia and guanidine are determined by titrating an aliquot of the preparation dissolved in glacial acetic acid with perchloric acid. A second aliquot is titrated in a methanol solution with sodium methylate. In the latter case only nitric acid combined with ammonia and not with guanidine is determined. Dicyandiamide does not interfere with either the first or second titration. The guanidine content is determined by difference. The accuracy and reproducibility is similar to that normally attainable in potentiometric titration [49].

Determination of Organic Anhydrides and Acids in Mixtures. The use of nonaqueous titration permits the possibility of determining the anhydrides of organic acids in mixtures with the acids [45]. Anhydrides of organic acids react with sodium methylate, a molecule of the salt and a molecule of ester being formed. Anhydrides give two molecules of acid or the salt respectively with water or aqueous sodium hydroxide solution. This means that it is possible to calculate the anhydride content.

Determination of Sodium and Potassium. We have used titration in nonaqueous media for determination of sodium and potassium in the course of their normal analysis [50]. After separating them completely in the form of their chlorides, the latter are converted into the acetates by means of mercurous acetate. The solution of sodium and potassium acetate in glacial acetic acid is then titrated with perchloric acid, using glass and calomel electrodes. It is possible in this way to determine 10-100 mg of sodium and potassium with an accuracy of 1-2%.

Redox Reactions

Titration in nonaqueous media has also been used for oxidation–reduction reactions. Most of the work in this field has been carried out by Tomicek et al. [23, 34, 26]. They have used solutions of bromine, trivalent titanium chloride, chromium trioxide, sodium permanganate, lead acetate, chloramine, and vanadium acetate in glacial acetic acid as titrants.



Curves obtained during titration of the 8-hydroxyquinolate of quinquevalent vanadium in a solution of $CHCl_3 + CH_3OH$, using as titrant a solution of divalent chromium acetate in dioxane, and using bimetallic electrodes.

Using extraction of the compounds of organic reagents with inorganic ions, we have shown that it is possible to carry out a direct titration of some of the complexes formed, in the medium of the extractant, not only with an aqueous solution of divalent chromium sulfate as a reducing agent for determining U^{VI}, Cr^{VI}, and Fe^{III}, but also with a solution of divalent chromium sulfate in dioxane [52, 53].

Divalent chromium acetate (~ 0.03 N) in dioxane is prepared as follows. An aqueous solution of divalent chromium chloride is added to a saturated solution of sodium acetate. The red, crystalline precipitate is filtered off, washed with water and dioxane, and then dissolved in dioxane. All the work is carried out in a special vessel in an atmosphere of N_2. The solution is stored in a CO_2 atmosphere.

All the measurements are carried out with a' "Radiometr pH M-22" pH meter, or with the Polish apparatus "Piezoelektronika". Titration is carried out in a special apparatus similar to that described by Zarinskii [54].

We tried out a calomel—platinum electrode as well as bimetallic electrodes: graphite, gold, platinum, tungsten, and tantalum. In Fig. 3 are shown titration curves obtained on using various pairs of electrodes with the 8-hydroxyquinolate of quinquevalent vanadium in a chloroform-methanol mixture, using a solution of divalent chromium acetate in dioxane as titrant. As is evident from the curves, the best electrodes proved to be the bimetallic electrodes Pt-Ta, Au-Ta, and also Pt-C and Au-C.

Determination of Copper, Vanadium, Uranium, and Molybdenum. To a chloroform solution of the 8-hydroxyquinolates of the metals indicated is added 2 ml of concentrated sulfuric acid and an equal volume of methanol. Nitrogen (free from oxygen) is then bubbled through the solution, and the mixture titrated with a dioxane solution of divalent chromium acetate.

Under these conditions copper gives one potential jump corresponding to completion of the reduction Cu^{II}/Cu^{I}. When excess divalent chromium acetate is added to the solution, reduction to metallic copper proceeds very slowly.

Under these conditions vanadium gives two potential jumps, the first corresponds to completion of the reduction V^{V}/V^{IV}, while the second corresponds to completion of the reduction V^{IV}/V^{III}. Sexivalent uranium is only reduced to U^{IV} and gives one jump.

Molybdenum is reduced in two stages, Mo^{VI} to Mo^{V} and then Mo^{V} to Mo^{III}. Two potential jumps are observed.

Separate titration of copper and vanadium, and of vanadium and uranium is possible.

SUMMARY

The article is devoted to a review of titration of acids, bases, and reducing materials in nonaqueous media.

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••Original Russian pagination. See C. B. Translation.

INTRODUCTION OF GASES TO BE ANALYZED INTO THE ION SOURCE OF A MASS SPECTROMETER

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The development of a precision mass spectrometric method for recording the isotopic ratios of light elements from the gaseous phase for samples of natural origin has been the subject of previous articles [1, 2]. The suggested two-channel glass system makes it possible by means of magnetically operated valves to introduce, in succession, the sample and then the standard into the ion source. This enables one to compare the isotopic composition of two gases, and to record the difference between their isotopic ratios automatically on the recorder tape.

The two-channel system has now been essentially improved as a result of which it has become more compact and is more universal in its applications.

Two glass diaphragms with openings of ~ 50 μ each were fitted into the feeding channels of the two-channel system.

The fractionating effect of the diaphragm was investigated before carrying out the research. The experimental procedure was as follows. The same gas was introduced simultaneously into both of the feeding channels and the isotopic ratios of its masses recorded by successive switching of the valves. Naturally, in this case, the isotopic ratios for the masses of the same gas introduced into the mass spectrometer through two channels were the same.

The gas was then removed from one of the channels by means of a diffusion pump, while the gas was allowed to stay in the other channel throughout the experiment. After a certain time the gas which had been under test was compared with a fresh portion of the same gas in order to establish the distribution which had occurred in its isotopes on passing through the diaphragm. This was repeated several times.

TABLE 1

Fractionation of Sulfur Isotopes on Passing Through a Diaphragm of ~ 50 μ

In leakage time of SO_2 from the feeding channel into the mass spectrometer	Weighting (gain in weight) of S^{34}/S^{32} as a percentage of the original
0	0
1 hr 45 min	0.08
3 " 20 "	0.14
4 " 43 "	0.17
5 " 5 "	0.2
6 " 30 "	0.25
9 "	0.33

TABLE 2

Mass Intensities Corresponding to the Less Abundant Isotope for the Same Pressure of the Gases in Front of the Diaphragm

Test gas	Mass no. and isotopic combination	Peak value, mv
SO_3	a) 66, $S^{34}O_2^{16}$	3000
	b) 50, $S^{34}O^{16}$	1720
CO_2	a) 46, $C^{12}O^{16}O^{18}$	370
	b) 30, $C^{12}O^{18}$	32
CO	a) 30, $C^{12}O^{18}$	170

TABLE 3

Minimum Volumes of the Gases Being Tested which can be Used for Recording the Isotopic Ratios

Test gas	Ion	Volumes of the test gas, cm^3
CO	CO^+	0,6
CO_2	a) CO_2^+	0,28
	b) CO^+	3,2
SO_2	a) SO_2^+	0,03
	b) SO^+	0,061

It is clear from Table 2 that on passing through the diaphragm its isotopic composition becomes heavier at an average rate of 0.04% per hour. Since such enrichment occurs, each sample in turn should be compared with a fresh standard. For certain gases, particularly CO, as will be shown later, this is a particularly important factor.

Establishment of the relation between the intensities of the ion currents and the pressure of the test gases in the channel of the feeding system was necessary, because in a number of cases the volumes of the gases at our disposal were very small, particularly CO, and, accordingly, it was necessary to reduce to a minimum the parasitic volumes in the feeding system. On the other hand, recording of variations in the isotopic composition of the light elements in the case of natural objects requires that the minimum amount of test gas be present so as to obtain the requisite intensity of the mass peaks. The values of the ion currents of the less abundant masses 30 (CO^+), 46 (CO_2^+), 50, (SO^+), 66, (SO_2 +) during recording of the ratios of the corresponding pairs of isotopes with an accuracy of ± 0.02 % should be of the order of 400-450 mv.

The experimental procedure was as follows. SO_2, CO_2, and CO as the gases were separately introduced into the feeding channels in such amount that their pressure in front of the diaphragm was the same in each case and equal to 8×10^{-3} mm Hg. When this pressure was attained the values of the mass peaks corresponding to the less abundant isotopes were recorded. It was established that their intensity differed, on the one hand, because of differences in the distribution of S^{34} and O^{18} isotopes; while on the other hand it was observed that there is a relation between the value of the ion current and the mass, i.e., there is a different ionization capacity for CO_2, SO_2, and CO molecules. Results of these measurements are given in Table 2.

In order to carry out a single state comparison of the isotopic composition of oxygen it was necessary to have about 0.6 cm^3 of CO under conditions such that the parasitic volumes in the feeding system were reduced to a minimum. Using the results given in Table 2 it is possible to calculate the minimum volumes of other gases both for the main masses as well as for the fission masses. The results obtained are given in Table 3.

As already noted it is necessary to have about 0.6 cm^3 CO in order to carry out an analysis. In this connection it should be borne in mind that carbon monoxide, in contrast to CO_2 and SO_2, is not condensed by liquid air, and, accordingly, it is difficult to have it in an ampoule larger than that shown in Table 3. These results served as a basis for constructing a new feeding system.

A Three-Channel Feeding System. A two-channel feeding system is not efficient enough since, in order to compare the isotopic composition of each sample taken in order, it is necessary to introduce each time into the second feeding canal a fresh portion of standard gas, since the isotopic composition of the previous portion has changed.

Bearing this in mind, and also wishing to increase the output of the set up during mass analysis, a three-channel feeding system has been suggested in which parasitic volumes have been reduced to a minimum, and accordingly the maximum utilization factor of the test gas has been achieved The amount of the standard gas used up has been cut in half compared with that used in the two-channel variant of the feeding system.

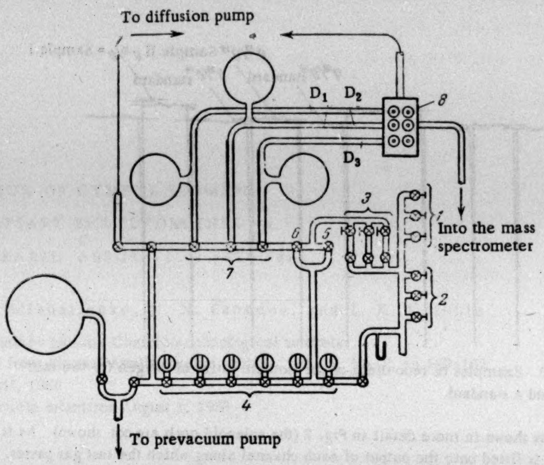
To diffusion pump
D$_1$
D$_2$
8
D$_3$
3
1
Into the mass spectrometer
6
5
7
2
4
To prevacuum pump

Fig. 1. Three-channel feeding system.

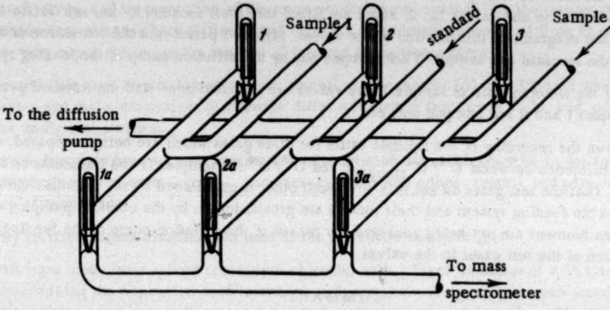
Sample I
1
2
standard
3
Sample II
To the diffusion pump
1a
2a
3a
To mass spectrometer

Fig. 2. Valve system.

The feeding system was prepared from glass mounted on a metal frame, and fitted onto the face plate of the vacuum part of the mass spectrometer.

Pumping down to the prevacuum pressure was carried out by the same pump as that used for evacuating the mass spectrometer. The high vacuum in the feeding system was established by a separate mercury diffusion pump.

The feeding system (Fig. 1) consists of many sections: 1) evacuated chambers for introducing the ampoules containing the test gases; 2) chambers in which is placed the acid for reacting with carbonates for CO_2 preparation; 3) a special attachment for small volumes of test gases (for CO and nitrogen samples). During the experiments these gases are introduced into the feeding channels along the shortest path by rotating the dosage taps mounted into the attachment; 4) traps for freezing out samples of CO_2 and SO_2 gases and for storing them prior to analysis; 5-6) dosage taps for introducing into the feeding channel the test gases which up to that point had been stored in traps 4; 7) the three feeding channels; 8) valve system; D_1, D_2 and D_3 are glass diaphragms with a diameter of 50 μ each.

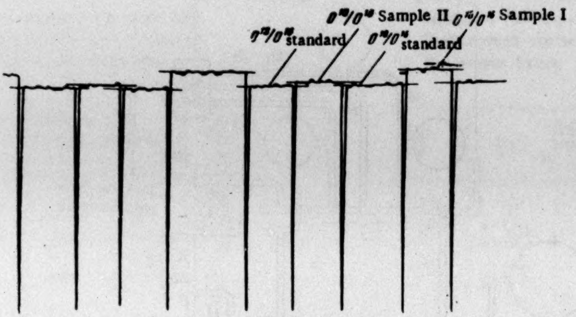

Fig. 3. Examples of recordings of the isotopic ratios of oxygen for two samples and a standard.

The valve system is shown in more detail in Fig. 2 (the solenoid coils are not shown). As is shown in the diagram a pair of valves is fitted onto the output of each channel along which the test gas passes. Their importance becomes clear when it is borne in mind that each of the three gases to be compared should pass separately into the ion source without mixing with one another, so that its isotopic composition is not distorted. Let us trace the movement of the gases in the case, for example, where sample I passes into the mass spectrometer. During the time that the three coils are switched on and valves 1a, 2, and 3 are lifted into their sockets, 1, 2a, and 3a are left closed. As can be seen from the diagram, in this position of the valves, sample I passes into the ion source of the mass spectrometer, while the standard and sample II are pumped out by the diffusion pump of the feeding system.

After recording the isotopic ratio of sample I, the valves are switched over. and the standard passes into the apparatus, while samples I and II are pumped out, etc.

In Fig. 3 is shown the recording of the isotopic ratios for three gases which are being compared, on the recorder tape. The difference between $O^{18}/O^{16}{}_{\text{standard}}$ and O^{18}/O^{16} for samples II and I amounts to 0.03 and 0.14%, respectively. That the test gases do not mix with each other is guaranteed by the fact that the contacts between the valves in the feeding system and their sockets are ground joints, by the constant pumping out of gases which at a given moment are not being analyzed, by means of the diffusion pump of the feeding system, and by the low pressure of the test gases in the valves.

SUMMARY

A study has been made of the fractionation of isotopes which occurs when a gas flows through a glass diaphragm fitted into the channel of the feeding system. The minimum volumes of gases have been established which are required in order to get ion currents which are sufficient for recording the changes in the isotopic composition of natural gases.

A description is given of the construction of a three-channel feeding system which permits simultaneous comparison of two samples with a standard.

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DETERMINATION OF CYMENE ISOMERS AND THE TERTIARY BUTYLTOLUENES BY THEIR INFRARED ABSORPTION SPECTRA

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Quantitative determination of the ortho-, meta-, and para-isomers in benzene derivatives by physical methods is exceptionally difficult on account of the similarity of the physicochemical constants of these components. Separation by chemical methods by means of sulfanilic acids [1], by means of the compounds of the alkylbenzenes with phthalic anhydride, and by separation of the corresponding keto acids [2] by the isotope dilution method [3], or the sulfonamide derivatives [4] are difficult, and require a considerable amount of time to carry them out. Accordingly, it is very expedient to use the method of infrared absorption spectra.

As Kaye and Otis have shown, taking xylene isomers as an example [5], the infrared absorption spectra of the ortho-, para-, and meta-derivatives of benzene differ sufficiently from each other, and, accordingly, they can be used for analytical purposes.

In the work described here we used the method of absorption spectrophotometry in the infrared for the quantitative determination of ortho-, meta-, and para-cymenes and ortho-, meta-, and para-tert-butyl toluenes in the presence of each other.

Specially purified carbon disulfide was used as the solvent in our work [6].

The cells were made from sylvite (potassium chloride) with a layer thickness of 0.09 cm. Calibration consisted in determining the absorption coefficients of each aromatic compound for each wavelength used in the analysis. Ortho-, meta-, and para-cymenes and tert-butyltoluenes were used for the calibration Para-cymene was obtained by a double distillation of the technical product in a distillation column of 17 theoretical plates. The meta-cymene was prepared by the Grignard reaction by the interaction of magnesium bromo meta-tolyl with isopropylbromide [7]. Ortho-cymene was prepared by the Würtz-Wittig reaction by the interaction of ortho-bromotoluene with isopropylbromide and sodium [8]. Para-tertiary butyltoluene was obtained from magnesium bromo-para-tolyl and tertiary butylbromide by the Grignard reaction [9], while meta- and ortho-tertiary-butyltoluenes were prepared in a similar fashion from the corresponding magnesium bromotoluenes [9].

The absorption spectra of the substituted benzene isomers studied are given in Figs. 1 and 2. The characteristics of these hydrocarbons are given in Table 1. From Figs. 1 and 2 it is evident that the spectra of the aromatic hydrocarbons differ significantly from each other. For determination of ortho-, meta-, and para-cymenes the most suitable wavelengths for analytical purposes proved to be (in μ): 12.28; 12.78; 13.21, while for ortho-, meta-, and para-tertiary butylbenzenes they were found to be 12.24; 12.75; 13.17 μ.

The apparatus was calibrated as follows: the optical density of each of the aromatic compounds was measured at the chosen wavelength in solution in carbon disulfide at suitable dilutions, and the extinction coefficients calculated.

TABLE 1

Refractive Indices of the Test Materials

Compound	n_D^{20}	
	found	published values
Para-cymene	1,4909	1,4908[10]
Meta-cymene	1,4930	1,4922[11]
Ortho-cymene	1,4989	1,5000[12]
Para-tertiary butyltoluene	1,4920	1,4936[13]
Meta-tertiary butyltoluene	1,4946	1,4946[13]
Ortho-tertiary butyltoluene	1,5067	1,5077[14]

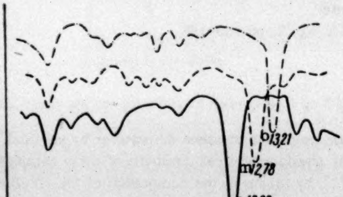

Fig. 1. Absorption spectra of the individual cymene isomers.

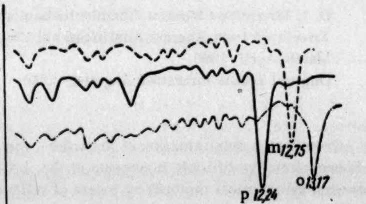

Fig. 2. Absorption spectra of the individual tertiary butyltoluene isomers.

The results obtained (Tables 2 and 3) show that the extinction coefficients observed depend on the concentration. This is explained by the fact that it is a narrow part of the spectrum that passes through the outlet slit of the spectrometer and not a strictly monochromatic beam. The insufficiently monochromatic character of the beam falling on the indicator determines the apparent deviation from the Bougere-Lambert-Beer law, which is strictly observed only in the case of monochromatic radiation [15].

The method of successive approximation was used in one form or another for determination of the concentrations of the components. The method used was that adopted by Kaye and Otis [5] for analyzing mixtures of xylene isomers. As an example, the analysis of mixtures of ortho-, meta-, and para-cymenes is considered. The optical density of the test mixture was measured at 12.28, 12.78, and 13.21 μ. Using the mean value of the

TABLE 2

Extinction Coefficients of Ortho-, Meta-, and Para-Cymenes at Various Wavelengths in Carbon Disulfide

Para-cymene				Meta-cymene				Ortho-cymene			
concentration, %	wavelength, μ			concentration, %	wavelength, μ			concentration, %	wavelength, μ		
	12,28	12,78	13,21		12,28	12,78	13,21		12,28	12,78	13,21
1,82	3,38	1,64	1,64	1,89	1,51	2,49	1,77	1,85	1,34	1,37	3,41
2,50	2,61	1,22	1,33	3,19	0,99	1,74	1,13	2,39	1,21	1,23	2,97
3,33	2,10	0,96	1,04	4,27	0,81	1,50	0,90	3,25	0,95	0,99	2,32
4,94	1,57	0,67	0,74	5,69	0,64	1,29	0,73	4,02	0,82	0,86	1,96
6,50	1,33	0,57	0,60	6,59	0,58	1,15	0,65	5,17	0,76	0,79	1,65
7,94	1,16	0,49	0,52	7,98	0,49	1,03	0,54	6,07	0,70	0,74	1,52
9,00	1,06	0,45	0,49	8,72	0,46	0,97	0,50	7,02	0,68	0,72	1,43
10,50	0,93	0,40	0,44	10,27	0,39	0,87	0,43	8,10	0,66	0,66	1,34

TABLE 3

Extinction Coefficients of Ortho-, Meta-, and Para-Tertiary Butultoluenes at Various Wavelengths

Para				Meta				Ortho			
concentration, %	wavelength, μ			concentration, %	wavelength, μ			concentration, %	wavelength, μ		
	12,24	12,75	13,17		12,24	12,75	13,17		12,24	12,75	13,17
1,21	3,54	1,63	1,83	1,62	1,17	2,18	1,22	1,23	1,34	1,30	2,19
2,05	2,63	1,09	1,10	1,78	1,16	2,12	1,20	1,56	1,33	1,28	2,10
2,16	2,59	0,97	1,04	2,47	1,09	1,80	0,92	2,03	1,09	1,05	1,83
2,50	4,46	0,87	0,91	3,01	0,76	1,69	0,83	2,61	0,87	0,86	1,53
3,61	2,04	0,63	0,65	3,19	0,73	1,63	0,79	2,79	0,85	0,85	1,52
3,82	1,96	0,60	0,61	3,97	0,60	1,44	0,72	4,30	0,55	0,54	1,21
4,35	1,85	0,53	0,54	5,16	0,50	1,29	0,60	5,77	0,43	0,42	1,02
5,14	1,57	0,43	0,44	7,44	0,33	1,00	0,50	8,08	0,32	0,32	0,86
6,25	1,52	0,39	0,39	8,82	0,31	0,97	0,45	9,63	0,28	0,18	0,79

TABLE 4

Results of the Analysis of Synthetic Mixtures of Ortho-, Meta-, and Para-Cymenes

Para, %			Ortho, %			Meta, %		
taken	found	absolute error	taken	found	absolute error	taken	found	absolute error
47,14	47,40	+0,26	53,85	53,60	—0,26	0,00	0,00	0,00
57,40	57,80	+0,40	6,16	5,60	—0,56	36,44	36,69	+0,16
64,40	63,70	—0,70	7,40	7,40	0,00	28,20	28,90	+0,70
75,40	76,00	+0,60	6,80	6,60	—0,20	17,80	17,40	—0,40
13,30	14,00	+0,70	29,00	28,60	—0,40	57,70	57,40	—0,30
7,50	7,20	—0,30	70,40	71,10	+0,70	22,10	21,70	—0,40
23,50	22,30	−1,20	2,50	2,90	+0,40	74,00	74,80	+0,80
17,00	16,10	—0,90	13,00	14,50	+1,50	70,00	69,40	—0,60
85,00	85,70	+0,70	10,00	9,56	—0,44	5,00	4,74	—0,26
88,90	89,20	+0,30	0,00	0,00	0,00	11,10	10,80	—0,30

TABLE 5

Results of the Analysis of Synthetic Mixtures of Ortho-, Meta-, and Para-Tertiary Butyltoluenes

Para, %			Ortho, %			Meta, %		
taken	found	absolute error	taken	found	absolute error	taken	found	absolute error
65,60	64,80	+0,80	34,40	35,20	+0,80	0,00	0,00	0,00
24,00	24,40	+0,40	0,00	0,00	0,00	76,00	75,60	—0,40
52,90	54,00	+1,10	13,70	13,00	—0,70	33,40	33,00	—0,40
77,00	76,70	—0,30	7,00	6,10	—0,90	16,00	17,20	+1,20
30,00	30,70	+0,70	65,00	65,30	+0,30	5,00	4,00	—1,00
43,90	44,95	+1,05	38,70	38,20	—0,50	17,40	16,85	—0,55
31,80	33,60	+1,80	20,00	19,10	—0,90	48,20	47,30	—0,90
31,00	32,00	+1,00	7,70	8,50	+0,80	61,30	61,50	+0,20
8,00	8,20	+0,20	52,00	52,25	+0,25	40,00	39,55	—0,45
12,00	12,35	+0,35	80,00	78,95	—1,05	8,00	8,70	+0,70

extinction coefficient of the isomers at these wavelengths, three equations of the following type were made up: $D_{cm} = (k_1c_1 + k_2c_2 + k_3c_3)x$; k_1, k_2 and k_3 are the extinction coefficients of the individual components; c_1, c_2, and c_3 are their concentrations; and $\underline{x}$ is the layer thickness.

By solving the equations obtained with respect to the concentrations, approximate values of the concentrations of the ortho-, meta-, and para-cymenes were determined. Three further equations were made up, but this time the values of the extinction coefficients taken from Tables 2 and 3 for the corresponding concentrations found were introduced into the equations.

The new set of equations were then solved again with respect to the concentrations. Since the values of the extinction coefficients used approximated to the true values, the values found for the concentrations were also appreciably close to the true value.

The method developed has been checked on synthetic mixtures of the appropriate hydrocarbons at various concentrations in carbon disulfide. The results obtained are given in Tables 4 and 5.

An analysis of a three-component mixture does not take more than 1-3 hours.

SUMMARY

Infrared absorption spectrophotometry has been used for the analysis of ortho-, meta-, and para-cymenes, and the tertiary butyltoluenes.

The mean relative error for the determination of the individual components in a three-component mixture of the para-, meta-, and ortho-cymenes is 1.5-2%, while for a three component mixture of the para-, meta-, and ortho-tertiary butyltoluenes this error is 2-3%.

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ISOLATION OF RADIOGENIC CALCIUM FROM MICA FOR ISOTOPIC ANALYSIS

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Ahrens [1, 2] determined the age of lepidolites by the calcium method and observed that lepidolite is the most suitable object for the calcium method, since this mineral is very poor in nonradiogenic calcium. As a result of experimental difficulties the calcium method has not been developed. In 1957 Polevaya, Titov, Belyaev, and Sprintsson [3] asopted the calcium method for determining the absolute age of sylvines; they developed a new technique for isolating calcium from sylvines and obtained interesting results. The results obtained for a series of samples coincide well with respect to the independent ratios Ar^{40}/K^{40} and Ca^{40}/K^{40}. The authors concluded that the calcium method can serve as a good control for the argon method. The present article is devoted to the development of a method for separating calcium from lepidolite and muscovite. According to Ahrens' scheme [1, 2] hydrofluoric acid and absolute alcohol are necessary for the separation. It is known, however, that commercial hydrofluoric acid contains up to 15 γ Ca per ml, and even distillation of the acid does not give a product of sufficient purity. Preparation of absolute alcohol also requires special operations. Accordingly, we refrained from using these reagents. We used pyrophosphoric acid, which was pure as far as calcium was concerned, for decomposing lepidolite and muscovite.

The method of determining silicon dioxide in the presence of silicates by means of pyrophosphoric acid [4, 5] is widely used at present. We used phosphoric acid for decomposing silicon containing samples.

Isolation of Calcium and Potassium. After bringing the samples into solution, the question arises of separating microgram amounts of calcium from a large amount of accompanying elements. The oxalate, fluoride, and other precipitation methods could not be used in view of the exceptionally low calcium concentrations. Accordingly, for such a separation, we used a chromatographic method [6, 7]. The cation exchange resin KU-2 in the H-form was used. On passing the test solution through a column of ion exchange resin, cations are adsorbed on the resin, while the anions pass into the filtrate. This makes it possible to separate phosphoric and silicic acids immediately. Subsequent washing with ammonia removes aluminum. Further washing with hydrochloric acid of various concentrations permits quantitative isolation and separation of potassium and calcium, potassium being eluted with 0.4 N hydrochloric acid, while calcium is eluted with 3-4 N hydrochloric acid.

In order to obtain reliable results, a study was made of the effect of various factors on the extent of the separation of potassium and calcium and on the purity of these elements; a check was also made on the relation between the adsorption of calcium and the phosphoric acid concentration (Table 1). The yield of calcium and potassium was controlled by means of radioactive indicators.

The effect of the phosphoric acid concentration on the adsorption of calcium on the column was studied with the aid of pure calcium salts (α = 10 mm, h = 130 mm, 5 g of KU-2). From the results given in Table 2, it is clear that calcium is readily adsorbed in the phosphoric acid concentrations range studied.

TABLE 1

The Relation between Calcium Adsorption and Phosphoric Acid Concentration

Phosphoric acid conc., %	Ca taken, mg	Ca found, mg	Difference, mg	Phosphoric acid conc., %	Ca taken, mg	Ca found, mg	Difference, mg
5	0,95	0,97	+0,02	18	0,95	0,98	+0,03
	0,95	0,93	−0,02		0,95	0,95	0
9	0,95	0,97	+0,02	18	0,95	0,97	+0,02
	0,95	0,93	−0,02		0,95	0,92	−0,03
14	0,95	0,95	0	22	0,95	0,93	−0,02
	0,95	1,10	+0,15		0,95	0,93	−0,02
15	0,95	0,97	+0,02				
	0,95	0,99	+0,04				

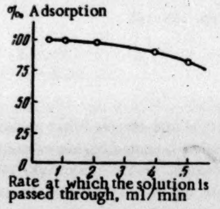

Fig. 1. Effect of the rate at which the solution is passed through the column on the adsorption of calcium by the KU-2 cation exchange resin.

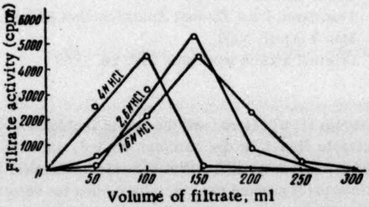

Fig. 2. Elution curves for the radioactive isotope Ca^{45} on the KU-2 cation exchange resin, on washing with varying volumes of hydrochloric acid with varying concentration.

It is clear from Fig. 1 that the rate at which the phosphoric acid passes through the column, apparently affects the adsorption of calcium. Adsorption on the column clearly decreases with increasing throughput of the acid. Obviously the rate at which the acid is passed through the column should not exceed 2 ml/minute.

In order to establish more accurately the completeness of the isolation, experiments were carried out on lepidiolite and on a synthetic mixture containing 85 g H_3PO_4, 2.29 g $Al(NO_3)_3 \cdot 9H_2O$, 0.0945 g KCl, and 0.0027 g $CaCl_2$. The radioactive isotope Ca^{45} (a β-radiator with an energy of 0.254 Mev) was used as the indicator. Measurements were made on a torsion β-counter. It was first of all necessary to establish the requisite concentration and the volume of acid to elute the calcium from the column. The elution curves of the radioactive isotope Ca^{45} on the KU-2 cation exchange resin on eluting with hydrochloric acid of varying concentrations and volumes are shown in Fig. 2.

It is clear from Fig. 2 that the volume of acid required to elute the calcium decreases with increasing acid concentration. The best results are obtained when the resin is washed with 150 ml of 4 N hydrochloric acid.

In order to establish the completeness of the separation of calcium from the samples when the suggested method is used, calcium whose Ca^{45} activity was known was added to an aliquot of the sample. The final filtrates after decomposition of the sample, and separation on a column, were measured for their activity on a β-counter.

It is clear from Table 2 that the yield exceeds 90%. The experiment on a synthetic mixture was also controlled by precipitation of calcium oxalate. Similar results were obtained.

Separation of Potassium from Calcium. In the mass spectrometric determination of radiogenic calcium, for establishing geological age by the calcium method, potassium interferes since it is superimposed on the Ca^{40}

TABLE 2

Ca^{45} added, cpm	Ca^{45} found, cpm	Yield, %
4110	3850	94
4110	4150	100
6750	6180	91
6750	6359	94
3815	3705	97

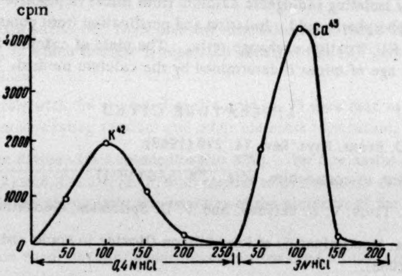

Fig. 3. Elution curves for the radioactive isotopes Ca^{45} and K^{42} on KU-2 cation exchange resin on eluting the column with hydrochloric acid.

peak. This necessitates complete separation of potassium and calcium. A number of methods have already been published for separating potassium and calcium during mass spectrometric analysis. Polevaya, Titov, Belyaev, and Sprintsson [3] have developed a method for separating the total amount of potassium from calcium contained in sylvine, by salting out with hydrochloric acid; their yield of calcium exceeded 90%. The chromatographic method not only permits separation of potassium and calcium, but also permits their separation from most of the accompanying elements. As indicated above, potassium is separated from calcium on the KU-2 cation exchange resin by eluting with 0.4 N hydrochloric acid. Completeness of separation was checked by means of the radioactive isotopes K^{42} and Ca^{45}, taking lepidolite as test material. The results obtained are shown in Fig. 3. The amount of acid used (ml) for elution is plotted along the abscissa, while the potassium and calcium concentrations (cpm) are plotted along the ordinate. This diagram clearly shows that on eluting the resin with hydrochloric acid of varying concentrations, complete separation of potassium from calcium is achieved.

The potassium yield is upwards of 95%. Final determination of potassium in the filtrate was carried out either flame photometrically, or gravimetrically by mean of magnesium dipicrylamate. The total calcium content was determined polarographically.

Separation Procedure. 1 g of sample was decomposed in 30 ml of freshly prepared pyrophosphoric acid in a quartz beaker at a temperature not higher than 250°, in the course of 5 minutes. The test solution was cooled to room temperature and diluted with twice-distilled water to 150-200 ml; the insoluble, free silicic acid was filtered off an a glass filter, and the filtrate introduced into a column 12 mm in diameter (20 g) cation exchange resin KU-2 in the hydrogen form) at the rate of 2 ml/min. After all the solution had passed through the column, the latter was washed with twice-distilled water until the filtrate gave a neutral reaction; aluminum was then eluted off the column with ammonia until the filtrate gave no reaction with alizarin S (a saturated solution of ammonia in twice-distilled water was used); the column was then washed again with twice-distilled water until the filtrate gave a neutral reaction. Potassium was next eluted from the column by 400 ml of 0.4 N (distilled) HCl, while calcium and the remaining cations were eluted from the column with 150 ml N HCl. After a double precipitation of iron and manganese with ammonia in the presence of hydrogen peroxide, the calcium in the filtrate was precipitated with oxalate.

Since lepidolite contains gamma amounts of calcium, for its mass spectrometric analysis it is necessary to take a sample of not less than 5 g; separation of calcium with oxalate is carried out in the combined filtrate. In order to determine calcium isotopes by the dilution method developed by N. I. Polevaya et al., a known amount of the stable isotope is added prior to decomposition of the sample.

In conclusion we should like to thank N. I. Polevaya and L. A. Khristianova for their advice.

SUMMARY

A method is suggested for isolating radiogenic calcium from micas (lepidolite and muscovite). The samples are decomposed with pyrophosphoric acid. Isolation and purification from potassium are effected by a chromatographic method using KU-2 cation exchange resin. The yield of calcium is greater than 90%. The above method is used when the age of micas is determined by the calcium method.

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ISOLATION OF RARE EARTHS FROM MINERALS

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For isolating the total rare earths (RE) from ores and minerals, use is made of the fluoride-oxalate method in its different variants [1, 2], in which thorium is separated with pyridine [3], potassium iodate [4], and, less frequently, hydrogen peroxide [5].

Results obtained previously with the acetonedioxalic acid [6, 7] were used as the basis of our work. Sodium p-aminosalicylate was used for separating thorium and other elements (zirconium, titanium) from the rare earths.

Precipitation of the Rare Earths with Acetonedioxalic Acid. The rare earths are precipitated by oxalate ions at a pH ranging from 6 [7] to 0.2-0.3 N [1, 2]* with respect to hydrochloric or nitric acids. The solubility product of the rare earth oxalates, particularly the oxalates of the elements of the yttrium group, is comparatively high [8, 9].

The solubility of the rare earth oxalates under the conditions used for their precipitation with calcium oxalate has not been studied sufficiently.

Completeness of the precipitation of the rare earths was studied as follows. To 100 ml of a solution of the rare earths with the pH values given in Table 1, was added 0.5 ml of a 28% solution of calcium chloride (25 mg Ca^{2+}) and 15 ml of a solution of acetonedioxalic acid [7]. The solution was boiled for 15-20 minutes, and the precipitate filtered on the next day through a "blue band" filter, 9 cm in diameter. To the filtrate was added a solution of calcium chloride containing 25 mg Ca^{2+}, the whole was mixed, and, after five minutes, the precipitate was filtered off through a "blue band" filter. Total rare earths in the first precipitate was determined by the usual gravimetric method using a microbalance [1, 5], while in the second precipitate they were determined photometrically [7].

It is clear from Table 1 that the rare earths are not quantitatively isolated as their oxalates when only one precipitation is carried out, while on carrying out a double precipitation it is possible to isolate appreciable amounts of the rare earths, particularly, if during the first precipitation, calcium oxalate is not used as a coprecipitant. Isolation of the rare earths was most complete when the initial pH was 6. The solubility of the rare earth oxalates increases with increasing acidity.

Similar experiments were carried out with elements of the yttrium group (Table 2).

It is clear from Table 2 that the rare earths as their oxalates are not quantitatively isolated when one precipitation is carried out. When a double precipitation is carried out it is possible to separate larger amounts of the rare earths than is possible with the rare earths of the cerium group under similar conditions (Table 1). Precipitation of the oxalates of the yttrium group is most complete at an acidity of 0.2 N with respect to hydrochloric acid. Coprecipitation with calcium oxalate increases the completeness of precipitation of the rare earths of this group.

Separation of Thorium, Zirconium, and Titanium from the Rare Earths by Means of Sodium p-Aminosalicylate. p-Aminosalicylic acid has been used for the determination of thorium [10, 11], with which it forms at a pH of 4-5 a water-insoluble compound $C_7H_6NTh(OH)_3$. p-Aminosalicylic acid is not ideal for the separation

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* As in Russian original.

TABLE 1

Precipitation of the Rare Earths of the Cerium Group in the Form of Their Oxalates. (Composition in %: Ce_2O_3-32.4; La_2O_3-20; Pr_2O_3-7.57; Nd_2O_3-25.7; Sm_2O_3-10.3; Gd_2O_3-2.2; Y_2O_3-1.66)

Acidity at the beginning of precipitation	Rare earths taken, mg	Rare earths found, mg		
		first precipitate	second precipitate	total
pH 6	4,62	4,52	0,13	4,65
pH 6	4,62	4,31*	0,19	4,50
pH 6	3,88	3,75	0,14	3,89
pH 6	7,89	7,59	0,17	7,76
pH 6	17,89	17,76	0,10	17,86
0,2 *N* HCl	4,62	4,30	0,21	4,51
0,2 *N* HCl	4,62	4,00*	0,26	4,26
0,2 *N* HCl	17,89	16,96	0,18	17,14
0,2 *N* HCl	17,89	17,13	0,17	17,30

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*Precipitation was carried out without addition of Ca^{2+}.

TABLE 2

Precipitation of the Rare Earths of the Yttrium Group in the Form of Their Oxalates. Composition in %: Y_2O_3-50.0; Yb_2O_3-20.0; Er_2O_3-10.0; Tb_2O_2-8.41; Ho_2O_3-4.0; La_2O_3-6.0

Acidity at the beginning of precipitation	Rate earths taken, mg	Rare earths found, mg		
		first precipitate	second precipitate	total
pH 6	4,99	4,54	0,34	4,88
pH 6	9,98	9,43	0,38	9,81
pH 6(without Ca^{2+})	4,99	4,38	—	4,38
0,2 *N* HCl	4,99	4,56	0,48	5,04
0,2 *N* HCl	9,98	9,62	0,38	1,00

of thorium from the rare earths, since it is almost insoluble in water [14]. The sodium salt of p-aminosalicylic acid is readily soluble in water and forms with thorium a compound corresponding to the formula indicated; at the same time the sodium salt can serve as a buffer (a 5% solution has a pH of 5). Experiments showed that it is possible to separate thorium, zirconium, and titanium from the rare earths by means of sodium p-aminosalicylate.

To 40 ml of a solution with a pH of 2-3 was added 1 g of sodium p-aminosalicylate. The solution was mixed, and then heated for 30 minutes on a water bath; the precipitate was filtered off through a "blue band" filter, 7-9 cm in diameter, and washed with 10 ml of a 0.5% solution of sodium p-aminosalicylate, the precipitate was then returned to the beaker in which the precipitation had been carried out, the precipitate being washed off the filter with 10-15 ml of the 0.5% solution of sodium p-aminosalicylate. The whole was stirred and, after 5-6 minutes, the precipitate filtered through a 7-9 cm diameter "blue band" filter. The precipitate was washed with the 0.5% sodium p-aminosalicylate solution until the total volume of the filtrate was 100 ml. To 100 ml of the solution was added 0.5 ml of calcium chloride (25 mg Ca^{2+}), and 15 ml of acetonedioxalic acid, and the whole boiled for 15 minutes and the volume made up to 100 ml.

On the next day the precipitate was filtered through a 7-9 cm diameter "blue band" filter. To the filtrate was added 0.5 ml of calcium chloride solution (25 mg Ca^{2+}), the whole mixed, and, after 5 minutes, the precipitate filtered through the same filter; the latter was then washed 5-6 times with a 1% oxalic acid solution.

The precipitate was ashed in a porcelain crucible at 600-700° and dissolved in 3-5 ml of concentrated hydrochloric acid, the solution obtained was evaporated to a volume of 0.5 ml, and the residue dissolved in 50 ml of water; excess ammonia solution was next added, the whole mixed, and, after one hour, the hydroxides were filtered and then washed with ammonia solution diluted 2-3 times, the hydroxides were finally dissolved in 10-15 ml of 5% hydrochloric acid and again precipitated with ammonia. The precipitate was ashed, calcined to constant weight, weighed, and the content of the rare earths calculated.

In the first two experiments precipitation of the rare earths was effected with oxalate in the presence of sodium p-aminosalicylate (1.5 g) which does not affect the quantitative separation of the oxalates, as is evident from a comparison of the results given in Table 3 with those given in Table 1. Up to 100 mg of thorium can be separated with a permissible error, from 4.62 mg of the rare earths. Zirconium and titanium which also form insoluble compounds with sodium p-aminosalicylate, entrain appreciable amounts of the rare earths. Their presence during the separation of thorium in amounts greater than 2 mg leads to large losses of the rare earths.

Separation of the Rare Earths from Minerals. Certain minerals containing the rare earths and not containing zirconium, titanium, niobium, and tantalum were decomposed with acids as described in the textbooks [1, 2, 5], after which their hydroxides were separated with sodium hydroxide, the hydroxides were then dissolved in 5%

TABLE 3

Separation of Thorium, Zirconium, and Titanium from the Rare Earths of the Cerium Group by Means of Sodium p-Aminosalicylate

Taken, mg				Rare earths
Th	Zr	Ti	rare earths found, mg	
—	—	—	17,89	17,13
—	—	—	17,89	17,86
20,0	—	—	4,62	4,58
30,0	—	—	4,62	4,26
50,0	—	—	4,62	4,35
100,0	—	—	4,62	4,35
50,0	2,0	—	4,62	4,35
30,0	5,0	—	4,62	4,06
5,0	10,0	—	4,62	3,33
5,0	—	2,0	4,62	4,20
5,0	—	5,0	4,62	3,47

TABLE 4

Separation of the Rare Earths from Synthetic Mixtures and Minerals, and Tests for Their Purity

Main components, mg	Rare earths added, mg	Rare earths isolated, mg	Impurities found in the rare earths
Labradorite 100,0 TiO_2 10,0 ZrO_2 10,0 Nb_2O_5 10,0 ThO_2 50,0 PbO 2,0	4,62	4,76	[Th, Pb, Ti, Zr, Ca] Not detected Fe—40 γ Nb<30 γ
The same ThO_2 70,0 PbO 5,0	4,62	4,42	[Th, Pb, Ti, Nb, Zr, Ca] Not detected Fe_2 20 γ
Labradorite 100,0 Nb_2O_5 10,0 Ta_2O_5 5,0 PbO 13,0 ThO_2 30.0	4,62	4,16	[Th, Pb, Ti, Zr, Nb, Ca] Not detected Fe 10 γ
Monazite (No. 136) 100,14 (Cont. 0.60% Th)	—	12,42	The same ; Fe 10 γ
Monazite (No. 472) —99,66 (Cont. 3.80% Th)	—	53,17	The same ; Fe 10 γ

hydrochloric acid and the pH adjusted to 2-3; thorium was separated with sodium p-aminosalicylate and the rare earths determined as described above. In other cases, where the minerals are not decomposed with acids, and contained the elements indicated, it was necessary to employ fluoride decomposition. 20-100 mg of the mineral was fused in a platinum basin with 1-2.5 g of potassium bifluoride. After cooling, the melt was dissolved on heating in 20-25 ml of water, and 2.5 mg Ca^{2+} and 5-8 ml of hydrofluoric acid added. The precipitated fluorides of thorium, the rare earths, and other elements were filtered off (in this case polyethylene vessels or vessels covered with paraffin were used) through a 7 cm "blue band" filter, and washed 2-3 times with dilute hydrofluoric acid. The precipitate in the platinum basin was dried, calcined at 400°, and evaporated twice with 1 : 1 sulfuric acid and water.

TABLE 5

Determination of the Rare Earths in Minerals

Sample	Th content, %	Rare earths found, %		Relative error, %
		by the given method	fluoride-oxalate-pyridine method	
Khlopinite	2,42	18,07	18,18	— 0,60
Ferriteorite	12,0	4,55	4,1	+10,0
Monazite No.3	8,0	48,15 47,75	47,42	+ 1,10
Orthite	1,0	10,80 10,93	12,03	—10,3
Yttropyrazite	0,1	17,85 17,90	18,38	— 2,90
Monazite No.6	2,8	37,71 37,86	—	—
Thorite	40,0	3,92	3,68	+ 6,50
Monazite No. 136	0,60	12,40 12,52	12,25	+ 1,75
Monazite No. 472	3,80	53,17	53,0	+ 0,33

The acid was evaporated until the damp salts were obtained; these were dissolved in 50 ml water. When during this stage, an insoluble residue was obtained, it was filtered off, dried, calcined at 400°, and fused with 0.8-1 g of potassium pyrosulfate. The cooled melt was dissolved in 10 ml of 5% sulfuric acid and the filtered solutions combined. To the solution obtained was added 5% sodium hydroxide solution until the hydroxides were precipitated, and 2-3 ml of the sodium hydroxide added in excess. The solution was heated for 15-20 minutes on a water bath and the precipitate filtered off through a 7-9 cm diameter "blue band" filter. The hydroxides were washed 2-3 times with dilute sodium hydroxide and then dissolved in 20-25 ml of 5% hot hydrochloric acid, sodium hydroxide was added dropwise until the pH was 3 using Congo paper; thorium was separated with sodium p-aminosalicylate, and the rare earths determined as described above. Rare earths were separated from synthetic mixtures and from minerals by this method (Tables 4 and 5).

The impurities in the rare earths obtained were determined after dissolving them (25 ml), the determinations were carried out on 2-8 ml of the given solution. Iron was determined by means of thiocyanate [12], calcium by murexide [13], titanium by hydrogen peroxide [12], zirconium by alizarin [12], lead by dithizone [12], and thorium by arsenazo [6]. Calcium was found in all the samples but the amount of it present corresponded to 0.2-0.3 ml of a 0.002 M solution of Complexon, iron was also detected in amounts of 5-10 μg. In all cases complete separation was effected from zirconium, titanium, lead, and thorium. The isolated rare earths are suitable for further chromatographic separation.

Table 5 contains comparative experimental results obtained during determination of the rare earths by the given method and by the fluoride oxalate pyridine method.

It is clear from Table 5 that the given method gives reproducible and accurate results for the determination of rare earths in minerals (error ± 10%).

SUMMARY

It has been shown that the oxalates of the rare earths of the cerium and yttrium groups can only be separated by a double precipitation when they are crystallized together with calcium oxalate (as the coprecipitant). Sodium p-aminosalicylate is suggested for removing thorium from the rare earths. A method has been developed for separating the rare earths from the minerals.

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*Original Russian pagination. See C. B. Translation.

EXPRESS METHODS FOR THE SPECTROGRAPHIC ANALYSIS OF RARE ELEMENTS *

COMMUNICATION 1. ANALYSIS OF COMPLEX MIXTURES OF THE RARE EARTHS

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Chemical methods of analysis permit determination of the total amount of the rare earths and cerium, and allow group separation into the yttrium and cerium subgroups to be carried out. Accordingly, for the analysis of mixtures of the rare earths into separate components, physical and physicochemical methods are used.

Polarographic methods are not universal in their application, they only permit determination of some of the elements (Eu, Sm, Yb, and also Y). Absorption methods cover a large number of elements, but their application is limited for a number of reasons (mutual overlapping of absorption bands and lines, effect of foreign ions, comparatively low sensitivity, etc.). For determinations of trace amounts of the rare earths (e.g., in pure metals which are not so rare) sensitive luminescent and radioactive methods are the most suitable.

At the present time the main method of analyzing complex mixtures of the rare earths is the x-ray spectrographic method, thanks to its reliability and to the independence of the results obtained on the composition of the samples, to the simplicity of the spectra, to the small amounts of sample required, etc. Nevertheless, in some cases, the applications of this method too are limited.

As for spectrographic emission methods, despite a number of difficulties (the complexity of the spectra, mutual superposition of spectral lines) they also find wide application for the analysis of mixtures of the rare earths. A considerable number of papers has been devoted to the question of the spectrographic analysis of the rare earths [1-23]. However, in most cases, the techniques suggested are complicated, cumbersome, and take a long time. In some cases the complications introduced into the analytical technique are not always justified.

Our problem was to develop express methods which would permit rapid and reliable determination of all the individual rare earths in complex mixtures of varying composition. An attack on such a problem is justified on the one hand by the absence, at present, of such methods; and, on the other hand, by the acute need for rapid control of the separation of the rare earths.

The basis of the suggested method was the method of homologous pairs in its original form, which is widely used for the analysis of ferrous and nonferrous metals and alloys. It is the correct choice of the reference element and strong homology of the analytical pairs of lines that determine finally the reproducibility and correctness of the determination. The method used for introducing the sample into the source is also important, it should ensure that the sample is completely burnt in a comparatively short time, and should diminish the fractionation of the components of the sample.

Choice of the analytical pairs of lines was based on the following requirements: 1) the absence of possible mutual superposition of the rare earth lines, and also superposition by other elements (zirconium, iron, calcium, etc.); 2) a sufficiently high absolute and concentration sensitivity of the analytical lines of the rare earths; 3) location of the analytical lines in the narrowest spectral region; 4) the minimum distance between the lines

TABLE 1

Test element	Wavelength, A		Concentration range, %
	analytical line	reference line	
Lanthanum	4086,71	4085,66	1,0— 25,0
The same	4141,74	4140,01	10,0—100,0
Cerium	4137,65	4134,31	2,0—100,0
The same	4137,65	4140,01	2,0— 70,0
Praseodymium	4143,14	4140,01	2,0—100,0
The same	4143,14	4134,31	2,0— 75,0
» »	4222,98	4212,63	2,0–100,0
Neodymium	4109,07	4110,05	2,0—100,0
Samarium	4280,78	4273,52	2,0—100,0
The same	4280,78	4277,37	2,0— 65,0
» »	4279,67	4273,52	5,0—100,0
» »	4279,67	4277,37	5,0—100,0
Gadolinium	4225,85	4212,63	2,0— 60,0
The same	4225,85	4210,61	2,0— 40,0
» »	4098,61	4096,63	5,0—100,0
» »	4098,61	4099,31	5,0—100,0
Europium	4129,74	4134,31	0,3— 10,0
The same	4129,74	4140,01	0,3— 10,0
» »	4205,05	4210,61	0,3— 10,0
» »	4205,05	4212,63	0,3— 10,0
Terbium	4144,45	4140,01	2,0—100,0
The same	4144,45	4135,68	10,0—100,0
» »	4278,51	4273,52	3,0—100,0
» »	4278,51	4276,72	10,0—100,0
Dysprosium	4221,10	4210,61	1,0— 60,0
The same	4218,09	4212,63	3,0—100,0
Holmium	4103,84	4099,31	0,5— 20,0
The same	4103,84	4096,63	0,5— 15,0
» .	4163,03	4179,81	0,5—100,0
Thulium	4105,84	4096,63	0,2 – 20,0
The same	4105,84	4099,31	0,5— 20,0
» »	4199,92	4210,61	20,0—100,0
» »	4199,92	4212,63	20,0—100,0
Yttrium	4142,84	4135,68	1,0— 30,0
The same	4142,84	4140,01	1,0— 7,0
» »	4251,21	4273,52	30,0–100,0
Eerbium	3692,65	3718,84	2,0— 30,0
The same	3616,57	3607,38	15,0—100,0
» »	3499,10	3499,58	10,0— 70,0
Ytterbium	3694,20	3678,91	0,1— 5,0
The same	3694,20	3698,17	1,5— 50,0
Lutecium	3567,84	3554,07	2,0— 50,0
The same	3567,84	3558,96	4,0— 50,0
» »	3554,43	3554,07	4,0— 50,0
» »	3554,43	3558,96	8,0— 50,0

and separate homologous pairs; 5) a minimum number of homologous lines ensuring complete coverage of the test concentration range; 6) high homology of the analytical pairs of lines.

The criterion for the homology of the analytical pairs of lines was that the relative blackening of the pair of lines for a given concentration should be constant when the discharge conditions are altered (current strength, arc gap, etc.). The degree of homology of the pairs of lines was established by the method of objective photometric measurement (using a microphotometer) of the spectrograms taken under various discharge conditions. In addition, the degree of homology of the pairs of lines was also checked on the basis of the constancy of the photometric evaluations as reflected in the analytical criteria on switching from one photographic plate to another.

The analytical criteria were established statistically by photographing and visual-photometrically measuring on a spectroprojector a large number of spectra of standard samples (8-10 plates to each standard). The correctness of the analytical criteria were checked, in addition, by constructing calibration curves (within the coordinates: photometric value—logarithm of the concentration of the rare earth) which were linear.

TABLE 2

Determination of Cerium

CeO_2, %	λ Ce—4137,65A	
	λ Zr—4134,31A	λ Zr—4140,01A
2,0	—4,0	—3,0
3,0	—3,0	—2,0
5,0	—2,0	—1,0
8,0	—1,0	0
12,0	0	+1,0
20,0	+1,0	+2,0
30,0	+2,0	+3,0
45,0	+3,0	+4,0
70,0	+4,0	+5,0
100,0	+5,0	

TABLE 3

Determination of Yttrium

Y_2O_3, %	λ Y—4142,84A		λ Y—4251,21A
	λ Zr—4135,68A	λ Zr—4140,01A	λ Zr—4273,52A
1,0	—3,0	+1,0	
1,6	—2,0	+2,0	
2,5	—1,0	+3,0	
4,0	0	+4,0	
7,0	+1,0	+5,0	
12,0	+2,0		
20,0	+3,0		
30,0	+4,0		—4,5
50,0			—3,5
70,0			—2,5
100,0			—1,5

As the result of experiments which were based on achieving maximum sensitivity of determination, stable and complete burning of the test material in a comparatively short time, and a rational ratio between the blackenings of the analytical lines (on the sensitivity threshold) and the background, the following analytical conditions were adopted.

1. **ISP-51 spectrograph with UF-85 camera (for the elements La, Ce, Pr, Nd, Sm, Gd, Eu, Tb, Dy, Ho, Tu, Y)**

ISP-51 spectrograph with UF-85 camera (for the elements La, Ce, Pr, Nd, Sm, Gd, Eu, Tb, Dy, Ho, Tu, Y)	**KS-55 with glass optics (for the elements Er, Yb, Lu)**
operating part of the spectrum 4080-4280 A	**3500-3700**
slit width 20 μ	**10 μ**
slit illumination—three lens	**three lens**
diaphragm size—circular	**circular**
8-stage attenuator	**8-stage attenuator**

2. **Excitation source—activated ac arc. Current—8 amp.**
3. **Preparation of the sample—mixtures of the rare earth oxides and zirconium oxide (reference element) were ground up in the ratio 1 : 4 (respectively).**
4. **Introduction of the sample into the spectrum excitation source—a thin layer of the sample was smeared on the grooved face of the lower copper electrode 4 mm in diameter (the upper electrode was ground to blunt cone) and the sample kept in position by means of a bakelite lacquer.**
5. **Exposure of the photographic plate—3 minutes.**
6. **Photographic plates—spectrographic type II, sensitivity 16 GOST units.**
7. **Treatment of the plates developed in type D-19 developer for 3-4 minutes at 20°.**
8. **The analytical pairs of lines and the test concentration ranges are given in Table 1.**

The analytical criteria for the determination of cerium, yttrium, and thulium are given in Tables 2-4 to illustrate the method.

The method suggested was checked on a large number of samples of rare earth oxides of the most varied composition, in order to establish the reproducibility and reliability. In the course of this work it was found that the reproducibility of the method is characterized by an error of ± 10-20% (relative) for a single determination. The reliability of the method was checked by comparing the results obtained by means of it with the results of x-ray spectrographic analysis; good agreement was found (apart from some individual exceptions).

TABLE 4

Determination of Thulium

Tu_2O_3, %	λ Tu–4105,84A		λ Tu–4199,92A	
	λ Zr–4096,63A	λ Zr–4099,31A	λ Zr–4210,61A	λ Zr–4212,63A
0,2	—5,0			
0,3	—4,0			
0,5	—3,0	—5,0		
0,75	—2,0	—4,0		
1,2	—1,0	—3,0		
1,8	0	—2,0		
3,0	+1,0	—1,0		
4,5	+2,0	0		
7,0	+3,0	+1,0		
10,0	+4,0	+2,0		
15,0	+5,0	+3,0		
20,0	+5,5	+3,5	—2,0	—5,0
30,0			—1,0	—4,0
45,0			0	—3,0
65,0			+1,0	—2,0
100,0			+2,0	—1,0

The method is characterized by the speed with which a complete analysis of a complex mixture of the rare earths can be carried out. For example, analysis of one sample takes about 2 hours, while the analysis of four samples takes 4-5 hours.

On the basis of special experiments it was found that the use of various models of the same type of apparatus (various ISP-51 spectrographs, eight-stage attenuators, photographic plates) did not lead to any changes in the analytical criteria. Accordingly, the tables of the analytical criteria can be used for carrying out analysis in other laboratories on the recommended apparatus.

Notes: 1. The figures inside the columns indicate by how many stages the lines compared (photometrically measured) are separated from each other in a given homologous pair of lines, when equality of their blackenings has been achieved. In these columns the sign - in front of a figure signifies that the reference line (that of zirconium) has been taken at a more attenuated stage than the analytical line; while the sign + indicates that it was taken at a less attenuated stage; 0 signifies equality of blackening of the lines in a pair, taken at the same attenuation stage.

2. In those cases where equality of the blackening of the lines inside a pair was not realized by a whole number of stages, the photometric evaluation is expressed in the form of a fraction, with an accuracy of $^1/_2$ of a stage.

3. It is recommended that the stages of the lines which have low (gray) blackening be compared.

4. If a photometric value is obtained during the photometric measurement, which is not given in the table, then the concentration is determined by interpolation.

5. Establishment of the concentration of an element is carried out on the basis of association, i.e., on the basis of several photometric values (homologous pairs); the mean value is taken from several experimentally established values of the concentration.

SUMMARY

An express method has been developed for the complete analysis of complex mixtures of the rare earths, which is based on the use of the method of homologous pairs of lines, coupled with stepwise attenuation of the spectra.

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PHOTOMETRIC DETERMINATION OF THORIUM IN MONAZITES WITH ARSENAZO II REAGENT

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The known methods for the determination of thorium and monazites are long and difficult. The gravimetric as well as the photometric methods of determining thorium require that the thorium be separated beforehand from accompanying elements. Several methods have been recommended for effecting separation: precipitation of thorium with oxalates [1-6], iodates [5, 7-10], fluoride [5, 9, 11-13], phosphates [9, 10, 14], and organic acids [14-20]; separation by extraction with mesityl oxide [11, 13, 21] or by other solvents [3, 22, 23]. There are also some other methods [10, 24-26]. Phosphates, sulfates, the rare earths, and other elements interfere with the direct photometric determination of thorium in the solutions obtained after decomposition of monazites. When thorium is determined by means of the reagents recommended earlier, phosphates and sulfates in an acid medium cause very strong masking of the thorium, which cannot be tolerated, while higher pH values when the masking is weaker, aluminum, iron, the rare earths, and other elements react in the same way as thorium.

As things stood, therefore, it seemed to the authors that the new reagent arsenazo II, discovered earlier by one of us [27], might be of interest. The stable complex which is formed between thorium and arsenazo II in acid solutions permits one to do without preliminary separation of sulfates and phosphates. The reaction conditions are chosen so that almost all the other elements also do not interfere with thorium determination.

Arsenazo II(diphenyl-4,4'-diarsonic acid 3,3'-bis[< -azo-2> 1,8-dihydroxynaphthalene-3, 6-disulfonic acid]) could be regarded as a double arsenazo I, which has been recommended previously for the detection and determination of a number of elements [23, 28-33].

Arsenazo II is an almost black, crystalline powder which is soluble in water and in dilute acids to give solutions which have the same rose color as arsenazo I. The reagent is stable both in the solid form and in solution and can be kept indefinitely. Strong oxidizing or reducing agents destroy the reagent. In Fig. 1 are shown the light absorption curves for solutions of arsenazo I, arsenazo II, and also of the complex formed between thorium and arsenazo II.

With respect to selectivity and to the colors formed, the color reactions of arsenazo II, to a first approximation, are similar to the reactions of arsenazo I. Thus, in acid solutions, Th, Ti, Zr, U^{IV}, and Fe^{III} form blue-violet colors, while in weakly acid and neutral solutions Al, U^{VI}, Cr, Cu, the rare earths, and some other elements form colors of varying shades from brownish to pure blue. In contrast to arsenazo I, however, the colors with arsenazo II develop in more acid solutions.

With all elements, apart from those elements whose cations tend to give oxo ions (e.g., Zr, Al, Cr), the colors develop immediately, and subsequently remain almost constant for several hours or days. When there is insufficient reagent the solutions are less stable; under such conditions rapid deposition occurs of precipitates

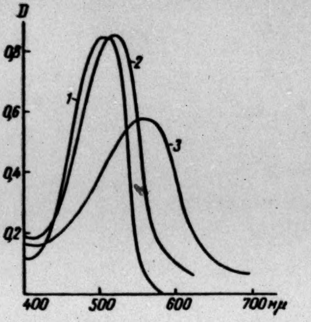

Fig. 1. Light absorption curves of solutions of arsenazo I (1), arsenazo II (2), and of the complex Th—arsenazo II (3). SF-4 spectrophotometer.

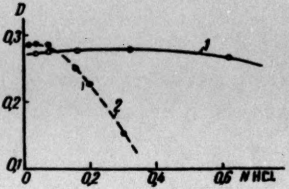

Fig. 2. Effect of acidity on the development of the color of the Th—arsenazo II complex (1) and Th—arsenazo I complex (2). Thorium concentration– 2×10^{-5} M, reagent concentration 2×10^{-4} M; λ 600 mμ; cell 10 mm.

which are the normal salts of the element with complex anions of the reagent. In order to prevent this, and to achieve the best reproducibility and accuracy during thorium determination, a 3-10-fold excess of reagent in molar proportions should be used.

Thorium ions react with arsenazo II in the molar ratio 1 : 1. The synthesis of this reagent has been described elsewhere [34].

Development of a Method for Determining Thorium

Decomposition of Monazite. When the thorium content of the monazite is of the order of several percent, and the sample is ground so that it passes completely through a 200 mesh sieve, on fusing a small aliquot of the monazite with potassium pyrosulfate for 5-7 minutes, complete extraction of thorium can be achieved. The residues which are formed during such a decomposition do not contain thorium. Other methods which have been suggested for decomposing monazite, such as: fusion with KHF_2 [11], with Na_2O_2 [9, 12, 26] or with KOH [37], heating with H_2SO_4 [1], $HClO_4$ [36], HF [34, 35],or with a mixture of $HClO_4$ + HF [3] take longer, or require further treatment of the solution to remove fluorides, etc.

Effect of pH. Within the range 0.01-0.6 N HCl, the light absorption of the complex formed between thorium and arsenazo II changes very insignificantly (Fig. 2). Accordingly, the choice of the optimum value of the acidity for thorium determination depends only on the following two factors: interference from other elements which interact with arsenazo II, and interference from anions which mask thorium. With decreasing pH the selectivity of the reagent increases, but, at the same time, the masking effect of phosphates and sulfates also increases. It was found that a concentration of 0.2 N hydrochloric acid appears to be suitable: under these conditions, the effect of almost all the elements is reduced to a minimum, while masking of thorium by phosphates and sulfates is still low.

An acidity of 0.2 N HCl is not the optimum in all cases. Thus, during determination of microgram amounts of thorium in the presence of the rare earths, it is better to dissolve the sample in H_2SO_4, and determine the thorium in a solution with a pH of 2.7. Under these conditions the sulfates do not mask thorium at all, while the earth elements do not give a color reaction with arsenazo II. On the other hand, in the absence of sulfates, and where it is necessary to determine thorium against a background of 1000-10,000 times its amount of Al, U^{VI}, Fe and other elements, the determination must be carried out at a higher acidity, e.g., in 0.6 N HCl.

Effect of Anions. Sulfates, which are usually present in solution in appreciable concentrations, always mask thorium to some extent. The extent of masking depends on the concentrations of the sulfates and the

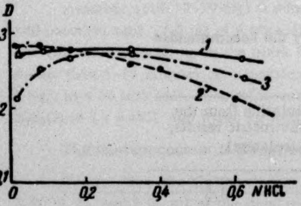

Fig. 3. Effect of acidity on development of the color of the Th–arsenazo II complex in pure solution (1), and in the presence of sulfates (2), and phosphates (3). Thorium content 50 μg; arsenazo II 2 mg; Na_2SO_4 0.2 g; $NaH_2PO_4 \cdot 2H_2O$ 2 mg; volume 10.0 ml; λ 600 mμ; cell 10 mm.

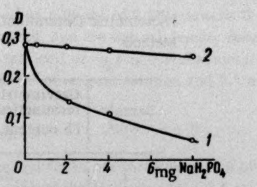

Fig. 4. Effect of phosphates during thorium determination with arsenazo I (1) and arsenazo II (2). Thorium content 50 μg; reagent 2 mg; medium 0.2 N HCl; volume 10.0 ml; λ 600 mμ; cell 10 mm.

TABLE 1

Effect of Accompanying Elements on the Determination of Thorium with Arsenazo II. 10 ml of Solution Contained 50 μg Th, 2 mg arsenazo II, 20 mg $K_2S_2O_7$; 5 mg $KH_2PO_4 \cdot 2H_2O$. Acidity 0.2 N with respect to HCl

Element	Permissible ratio of thorium : :element
Ti	1 : 0,2
Zr	1 : 0,3
Nb, Ta	1 : 0,4—0,8
Fe^{III}	1 : 0,5
Cr^{III}	1 : 0,5
Mo, V, W	1 : 0,2—1
U^{VI}	1 : 4
Al	1 : 50—100
K, Na, Ca, Mg, Σ RE, Fe^{II}	1 : 1000—10 000

reagents, and on the pH of the solution (Fig. 3). It was found that at a reagent concentration of 0.0002 M, a HCl concentration of 0.2 N, and a sulfate content of the order of 1-5 mg/ml, thorium is masked to the extent of 5-7%. However, even this value can be automatically taken into account, if when the procedure described is followed, the sulfate concentration is kept the same in the test solutions and in the solutions used for constructing the calibration curve.

Phosphates also mask thorium to some extent. The extent of the masking depends on the phosphate and reagent concentrations, and on the acidity of the solution. It has been found that the effect of phosphates can be reduced to a minimum by determining thorium in a medium of 0.1-0.4 N with respect to HCl (Fig. 3). When thorium is determined in a medium of 0.2 N HCl, and the phosphate content is 1-2 mg/ml, the error in the thorium determination does not exceed 2-3% (Fig. 4). This corresponds to a ratio of Th : P_2O_5 = 1 : 50-100. The usual P_2O_5 content of monazites is 25-30% [35]. Accordingly, direct determination of thorium in monazites is still possible as long as the thorium content is not less than 0.5%.

Fluorides mask thorium considerably, but they are fairly completely removed during decomposition of monazites with $K_2S_2O_7$. This was checked by adding large amounts of fluoride to monazite samples.

Effect of Other Elements. Elements whose cations hydrolyze at pH ≫ 2 (alkali metals, alkaline earth metals, rare earths, Al, Cu, Fe^{II}, etc.) do not interfere appreciably even when the amounts of these elements present are hundreds and thousands times the amount of thorium

Zirconium and titanium react similarly to thorium. Usually, however, the content of these elements in monazites is so small (< 0.02 % [35]), that the interference they cause can be disregarded. Moreover, it has been found that moderate amounts of zirconium and titanium efficiently mask phosphates, and have been specially introduced into the test solution for this purpose. The masking of thorium itself (~ 5%) as indicated already can be automatically taken into account. Data on the effect of the most important elements on thorium determination are given in Table 1.

TABLE 2

Photometric Determination of Thorium in Monazites by the Recommended Method

Sample No.	Gravimetric determination of Th content, %	Th found by the recommended method, %	Deviation from the gravimetric results, % (relative)
1	7,37	7,12	−3,5
		7,33	−0,5
2	7,19	6,9	−4,0
		7,03	−2,4
		7,14	−0,7
3	7.04	7,25	+2,7
		7,21	+2,2
4	6,05	6,07	+0,3
		6,1	+0,8
5	5,41	5,21	−2,5
		5,14	−3,7
6	1,83	1,75	−4,3
		1,78	−3,3
7	0,73	0,70	−4,2
		0,71	−2,7

Phosphates, sulfates, and other anions exhibit a considerably weaker effect during determination of thorium with arsenazo III−1,8-dihydroxynaphthalene-3,6-disulfonic acid-2,7-bis[< -azo-2-> -phenylarsonic acid]−a reagent which one of us prepared in 1959 [36]. Many other elements also do not interfere. The exceptions are the rare earths, which interfere appreciably when arsenazo III is used. Accordingly, for the analysis of monazites which contain up to 20-30% total rare earths, the use of the reagent arsenazo II is preferable.

Accuracy of the Method and the Time of Determination. During determination of thorium in monazites the experimental error does not exceed 3-5% relative; while for determination in pure solutions the error is 1-2% relative.

The method described below was checked on monazite samples containing 4-7% of thorium, and on synthetic mixtures containing 0.5-2% of thorium; these mixtures were prepared by mixing monazite, phosphorite, and preparations of the rare earths.

One determination takes 25-30 minutes. Results of thorium determinations are given in Table 2.

Determination of Thorium in Monazites. Reagents Required. A standard thorium nitrate solution containing 50 μg Th/ml; a 0.1% aqueous solution of arsenazo II; a 0.5% solution of sodium phosphate ($NaH_2PO_4 \cdot 2H_2O$); a 2% solution of $K_2S_2O_7$ in HCl 1 : 5.

EXPERIMENTAL PROCEDURE

A 10-200 mg aliquot of finely ground monazite containing 0.5% and upwards of thorium is placed in a quartz test tube and fused with 2.0 g of potassium pyrosulfate over the small flame of a blowtorch, for several minutes, first with gentle heating and subsequently at a dark-red heat. The melt is dissolved in 40 ml of 1 : 1 HCl. The solution obtained should be almost colorless. The presence of heavy particles which separate out rapidly on the bottom of the tube indicates incomplete decomposition.

The solution is quantitatively transferred to a 100 ml standard flask in which it is made up to the mark with water and thoroughly mixed. The solution is allowed to stand, or part of the solution is filtered into a dry flask. A 2.5 ml aliquot (25-250 μg Th depending on the original aliquot taken) is pipetted into a 25 ml standard flask. For the analysis of monazites containing more than 10-15% Th, a smaller aliquot is taken. In this case, at the same time, potassium pyrosulfate in the form of its 2% solution in 1 : 5 HCl (up to 2.5 ml) is added to bring its level up to the requisite value.

Ascorbic acid (10-20 mg) is added to the same flask. If iron is known to be absent there is no need to add ascorbic acid. 2.0 ml of 0.5% sodium phosphate is added, followed by 5.00 ml of 0.1% arsenazo II solution, and the volume made up to the mark with water. The contents are mixed, and the optical density measured not sooner than 5-10 minutes on a spectrophotometer at 600 mμ in a 10 mm cell or on a photocolorimeter with a red filter, in a 50 mm cell. The reference solution is one containing 5.00 ml of reagent solution and 2.5 ml of $K_2S_2O_7$ in 1 : 5 HCl, and made up to 25 ml with water.

The thorium content is determined by means of a calibration curve.

Construction of a Calibration Curve. Into a series of 25 ml standard flasks are introduced 0, 0.50, 1.00, 2.00, 4.00, and 6.00 ml of the standard thorium nitrate solution. To each of the flasks is added 2.5 ml of the solution of $K_2S_2O_7$ in 1 : 5 HCl, 2.0 ml of sodium phosphate solution, and 5.00 ml of arsenazo II solution. The volumes are made up to 25 ml with water, the contents of the flasks mixed and the optical density measured not sooner than 5 minutes after mixing (the same reference solution is used). A light absorption–thorium concentration curve is constructed.

SUMMARY

A method is described for the photometric determination of thorium in monazites by means of arsenazo II; the determination is carried out immediately after decomposition of the monazites without separation of thorium from impurities.

Phosphates (up to 30% P_2O_5), Zr, Ti, Mo, V, W (up to 0.2-0.5%), the rare earths, and other elements do not interfere. A determination takes 25-30 minutes; the error is not greater than 3-5% (relative).

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GRAVIMETRIC SEMIMICRO DETERMINATION OF VANADIUM BY MEANS OF β-HYDROXYNAPHTHYLALETHYLAMINE AND β-HYDROXYNAPHTHYLALDOXIME

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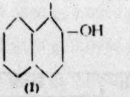
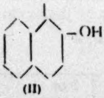
We have demonstrated the possibility of using β-hydroxynaphthoic aldehyde in analysis previously [1-4]. Kuznetsov [5] has established that many organic compounds with a phenolic hydroxyl in the molecule are capable of interacting with quadrivalent vanadium to form intracomplex compounds. Kul'berg [6] has deduced that the general functional analytical group for quadrivalent vanadium is $K_c^{*}-\overset{|}{\underset{|}{(C)}}_n-\underset{\|}{C}-OH$, where K_c is the complex-forming group.

Bearing in mind that this combination of atoms with active functional groups occurs in β-naphthoic aldehyde, in the work described here, we have suggested the determination of vanadium by various derivatives of this aldehyde.

As a result of our studies, methods have been developed for the quantitative determination of vanadium with β-hydroxynaphthylalethylamine (I) and β-hydroxynaphthylaldoxime (II).


(I)


(II)

EXPERIMENTAL

Synthesis of β-Hydroxynaphthylalethylamine. 1.5 g of ethylamine was dissolved in 10 ml of water, and 10 ml of a 9% sodium carbonate solution added. The solution obtained was place on a water bath and 20 ml of a 12.5% alcoholic solution of β-hydroxynaphthoic aldehyde added to it dropwise. After cooling, greenish-yellow, acicular crystals of β-hydroxynaphthylalethylamine separated out. The product was recrystallized from alcohol. The melting point was 123°.

Quantitative Determination of Vanadium with β-Hydroxynaphthylalethylamine. To an ammonium vanadate solution containing 1 mg vanadium/ml was added the same volume of a 2% alcoholic solution of β-hydroxynaphthylalethylamine. The liquid was heated to the boil and ascorbic acid crystals added at the rate of 20 mg to each mg of vanadium. A yellow-greenish, crystalline precipitate of vanadyl β-hydroxynaphthylalethylamine

TABLE 1

Weight of precipitate, g	Vanadium found, mg	Theoretical amount of vanadium, mg	Error	
			mg	%
0,0092	1,01	1,00	+0,01	+1
0,0186	2,05	2,00	+0,05	+2,5
0,0272	2,99	3,00	—0,01	—0,3
0,0364	4,00	4,00	±0,00	—0
0,0456	5,02	5,00	+0,02	+0,4

separated out immediately. The precipitate was filtered off through a No. 4 glass crucible, washed three times with 50% alcohol, and then dried at 110°. The conversion factor to vanadium is 0.10995.

The resultsgiven (Table 1) show that vanadium can be quantitatively determined by the method described. The experimental error lies within the permissible errors of gravimetric analysis.

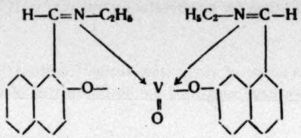
Analysis of the Compound Obtained

Aliquots taken: 0.1692 g; 0.1660 g; V_2O_5 obtained 0.033 g; 0.0324 g.

Aliquot taken; 1.055 g; N found 6.11%

Calculated for $[C_2H_5N = CH-C_{10}H_6O]_2VO$; 10.99 V%; 6.02 N%.

From these results the formula of the compound obtained can be represented as follows:



The method used for determining vanadium in synthetic mixtures in the presence of trivalent iron was the same as that used for pure vanadium solutions.

The results obtained are given in Table 2.

TABLE 2

Vanadium, taken, mg	Iron added, mg	Vanadium found, mg	Error	
			mg	%
2,00	4	2,07	+0,07	+3,5
2,00	4	1,96	—0,04	—2,0
2,00	2	1,96	—0,04	—2,0
3,00	3	3,06	+0,06	+2,0
3,00	3	3,01	+0,01	+0,3

Determination of Vanadium in Ferrovanadium. A sample of ferrovanadium containing a known amount of vanadium (34.96%) was used for vanadium determination. 0.2603 g of ferrovanadium was dissolved in nitric acid (sp. gr. 1.2), the solution was heated to remove nitrogen oxides, and was then neutralized with 25% ammonia solution and made up to 100 ml (vanadium content 0.91 mg/ml). Known aliquots of this solution were taken for vanadium determination. In addition, in some cases, additional amounts of vanadium were added.

TABLE 3

Volume of the ferrovanadium solution, ml	Vanadium content, mg	Vanadium added, mg	Vanadium found, mg	Error	
				mg	%
4	3,64	--	3,61	+0,03	+0,82
4	3,64	--	3,65	+0,01	+0,27
3	2,73	1,97	4,79	+0,09	+1,88
3	22,7	1.97	4.71	+0,01	+0,21

The results obtained are given in Table 3.

Lead and copper interfere with determination of vanadium.

Quantitative Determination of Vanadium with β-Hydroxynaphthylaldoxime. To a known volume of ammonium vanadate solution containing 1 mg V/ml was added an equal volume of alcohol. To the solution, which was heated almost to the boil, was added the same volume of a 2% alcoholic solution of β-hydroxynaphthylaldoxime, to which had been added beforehand ascorbic acid dissolved in water, at the rate of 20 mg acid to each mg of vanadium. A gray-green, crystalline precipitate settled out immediately. After 30 minutes the precipitate was filtered off through a No. 4 glass crucible, washed three times with 50% alcohol, dried at 110°, and weighed. The conversion factor to vanadium is 0.11598.

It is clear from Table 4 that determination of vanadium by the method described gives satisfactory results.

TABLE 4

Vanadium taken, mg	Vanadium found, mg	Error	
		mg	%
2.00	1.97	-0.03	- 1.5
3.00	2.97	- 0.03	- 1.0
4.00	4.06	+ 0.06	+ 1.5

Analysis of the Compound Obtained

Aliquot 0.0960 g; 0.0200 g V_2O_5 obtained; 11.66% V found
0.2174 g; 0.0450 g V_2O_5; 11.59% V
0.9805 g; 0.0631 g N 6.43% N
1.0123 g; 0.0639 g N 6.31% N

On the basis of the suggested formula $(C_{11}H_8O_2N)_2VO$ the theoretical value for V is 11.6% and for N it is 6.38%.

Results for the determination of vanadium in ferrovanadium (34.96%), which was carried out by the method described, are given in Table 5. Additional amounts of vanadium were added in some cases.

Thus the method of determining vanadium in ferrovanadium by means of β-hydroxynaphthylaldoxime gives completely satisfactory results.

Nickel and copper interfere with the determination. Quadrivalent titanium at a concentration of 1 mg/ml forms a fine crystalline precipitate which is brick red in color; at low concentrations (5 μg Ti/ml) a yellow color is obtained.

TABLE 5

0.2860 g of Ferrovanadium in 100 ml Solution, 1 mg/ml

Vol. of ferrovanadium solution, ml	Vanadium content, mg	Vanadium added, mg	Vanadium found, mg	Error	
				mg	%
3	3,00	—	2,95	−0,05	−1,67
4	4,00	—	4,06	+0,06	+1,5
3	3,00	2,00	5,03	+0,03	+0,6
3	3,00	3,00	6,08	+0,08	+1,33

SUMMARY

New gravimetric methods have been developed for determination of vanadium in the form of $[C_2H_5-N=CH\cdot C_{10}H_6O]_2VO$ and $[HON=CHC_{10}H_6O]_2VO$ for which the respective correction factors to vanadium are 0.10995 and 0.11598.

By using ascorbic acid as a reducing agent vanadium can be determined in the presence of iron without preliminary removal of the latter.

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THE ANALYTICAL CHEMISTRY OF URANIUM

COMMUNICATION I. THE LUMINESCENT METHOD OF DETERMINING URANIUM

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The quantitative determination of uranium by the luminescent method is based on the capacity of melts of sodium fluoride, or fluoride-carbonate mixtures activated by uranium, to luminesce on being irradiated with ultraviolet light [1-4]. When the uranium concentration of the melt is less than 15-20 μg/g there is a linear relation between U concentration and the intensity of the radiation. The sensitivity of the method is limited by the existence of a residual radiation of the melt arising from uranium which has not been deliberately added; depending on the purity of the reagents used and the experimental conditions, this residual radiation may be equivalent to a uranium concentration of the melt amounting to 0.0001 to 0.02 μg/g [4].

Hitherto, the luminescent method has been used in those cases where maximum sensitivity or a rapid determination is necessary with a comparatively low accuracy. Increasing the accuracy of the method is connected not only with improving the techniques used for separating uranium from interfering impurities, but also with improvements in the techniques used for preparing luminescent samples, and improvements in the apparatus used for evaluating the intensity of the luminescence. With the introduction of photoelectric apparatuses into the practice of luminescent analysis, rapid variants of the luminescent determination have been developed in which the samples are not given a preliminary purification, but in which the test solution is diluted and known amounts of uranium are added [4-7].

The present article is devoted to descriptions of some improvements in the technique of determining uranium by the luminescent method.

Preparation of Luminescent Samples

Fluoride-carbonate melts are widely used for uranium determination. A fluoride-carbonate mixture consisting, for example, of 9% NaF, 91% $KNaCO_3$ [8] and mixed with the dry residue from the test solution, is fused in special platinum basins in the flame of a gas burner or in an electric oven [4].

After comparing various methods of fusing samples in a flame and in electric ovens, we concluded that the errors which are most difficult to eliminate are those connected with the effect of the atmosphere in which the fusion is carried out. This is particularly true for the case of flame fusion.

The atmosphere in electric ovens with exposed nichrome heaters proved to be unsuitable for preparing luminescent samples. It was also established that the use of ovens with insulated heaters does not exclude the possibility of very small sputterings of alloy and other materials on the internal ceramic surfaces; this can lead to contamination of the atmosphere in the oven and to a lowering of the reproducibility of the results.

As experiments showed, the most reproducible results are obtained with an oven provided with a renewable platinum case (Fig. 1), which is periodically washed. The temperature of the oven is kept at the required level by means of an autotransformer and a voltmeter graduated by means of a thermocouple. The oven can be readily made in the laboratory. It is suitable for mass determinations.

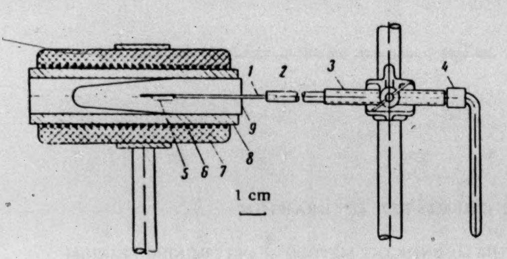

Fig. 1. Electric oven with renewable platinum case (1 cm corresponds to 3.5 mm). 1) Platinum rod; 2) glass rod; 3) glass tube; 4) rubber ring; 5) platinum basin; 6) nichrome spiral; 7) asbestos insulation; 8) porcelain tube; 9) platinum vessel (Smith crucible).

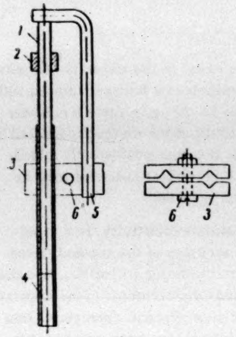

Fig. 2. Tube with piston. 1) Glass-rod piston; 2) rubber ring; 3) plastic jaw; 4) glass tube; 5) stop piece; 6) screw.

The luminescent disc is prepared as follows.

The residue of the evaporated test solution is covered in a platinum basin 5 with some of the melt or with a "blank" disc prepared beforehand. The basin is placed in the ring of the platinum rod 1 and is moved into the oven case. After a three minute fusion the melt is cooled and is removed from the basin. The disc is turned over and is fused again. Three of four fusions are necessary for the most uniform distribution of the uranium in the melt.

For mass determinations, a tube fitted with a piston (Fig. 2) enables one to dose out the melts rapidly and fairly accurately. The design suggested is more convenient than that used earlier by Price et al. [4] and is considerably easier to make than a similar design from stainless steel [9].

A glass rod acting as a piston 1 can be moved inside the glass tube 4. The stroke of the piston is determined by the rubber ring 2 and the stop 5, also made from a glass rod. By altering the mutual position of the stop and the tube clamped in the plastic jaw 3, it is possible to change the free volume of the tube. By rapid immersions of the end of the tube in the powder, the latter is packed into the free volume, from which it is forced out by means of the piston into the platinum basin. The dosage accuracy is on the average ± 1.5%.

When mass determinations are being carried out it is also convenient to use granulated reagent prepared by means of a special apparatus (Fig. 3).

Into a tubular oven which is connected into the circuit via a ferroresonance voltage stabilizer and an autotransformer, is placed a platinum vessel 4, the lower part of which is an extension with an internal diameter of 0.5 mm, external diameter 2 mm, and 12 mm long (the vessel is prepared from a Smith crucible and a section of a Dreschmidt platinum capillary). The outlet from the vessel through the capillary is stopped by means of the conical tip of a platinum rod 1 with a diameter of 1 mm. 27 g of $KNaCO_3$ and 3 g of NaF are loaded into the platinum vessel. After fusing, the mixture is carefully mixed with a piece of platinum wire for several minutes. After this the end of the platinum rod is removed from the capillary, and the mixture, in the course of two minutes, flows onto the surface of a massive steel disc 9, which is rotated by means of a SD-60 synchronous motor. After the granules have become cold they are scraped off with a scraper into a quartz flask. The weight of the granules is 110 mg and is reproducible to an accuracy of ± 1%. The granules possess high mechanical

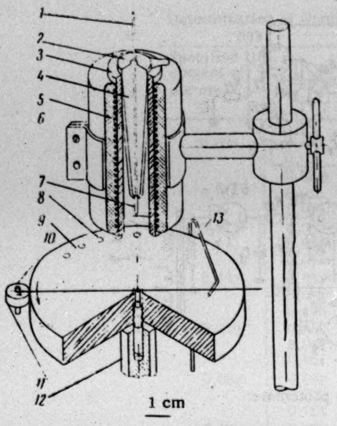

Fig. 3. Apparatus for preparing granules (1 cm corresponds to 3.5 mm). 1) Platinum rod; 2) platinum lid; 3) porcelain tube; 4) platinum vessel; 5) nichrome spiral; 6) asbestos insulation; 7) platinum capillary; 8) fluoride-carbonate drop; 9) steel disc; 10) axis of synchronous motor; 11) rubber pulley; 12) bearing; 13) scraper.

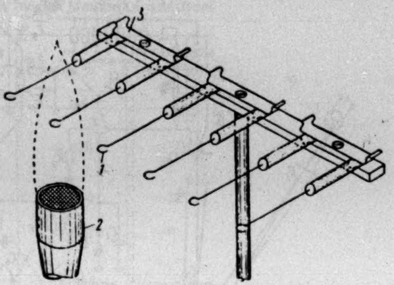

Fig. 4. Stand for holding rods with platinum loops: 1) Tablet; 2) burner; 3) spring.

stability and can be stored in closed weighing bottles indefinitely. The apparatus can also be used for granulating pure sodium fluoride. For this purpose some complications arise because of the high melting point of sodium fluoride.

The intensity of the luminescence of samples made from a pure solution of a uranyl salt is reproduced with an average relative error of 1.5-2%, when the melt is dosed with granules, or by means of a tube fitted with a piston, while the fusion is carried out in an electric oven with a platinum case.

In the express variant of the luminescent method of determining uranium, the samples are prepared in the form of beads, while uranium is introduced into the melt by immersing a "blank" bead in the test solution and then fusing it again. This technique can be improved by means of a simple apparatus, and by dosing the solution with drops. The apparatus consists of a tube fitted with a piston, a stand on which several rods with platinum loops can be fitted simultaneously, a forceps to the tips of which are fastened elastic petals made from foil, and a micropress of stainless steel for pressing portions of powder into tablets (a die cylinder 200 mm in diameter, and 300 mm long with an internal channel 4 mm in diameter, along which a plunger rod fitted on a massive base can slide).

Tablets of sodium fluoride (50 mg) are placed, by means of a forceps with soft tips to prevent the tablets from being crushed, on the platinum loops, and are fused in turn in the flame of a Mekker burner (Fig. 4). A drop of test solution is then placed on each tablet by means of a drop pipet or a micropipet. After drying in a stream of hot air, the tablets are fused in turn in the edge of the flame until the last crystal has disappeared. After some practice, the reproducibility of the preparation of tablets from a pure solution of a uranyl salt is about ± 6-7% instead of ± 15%, which is characteristic of the express method, in which dosing with the solution is carried out by immersing a "blank" bead in it.

It should be pointed out that the error in dosing the melt and the solution in the variant described does not exceed 2%.

The scatter of 6-7% is determined by variations in the conditions of fusing in the flame.

Measurement of the Intensity of Luminescence

The accuracy of a luminescent determination is determined to a very large degree by the method of measuring the luminescence intensity. Without any doubt photoelectric measurement [4, 10-12] is the most developed.

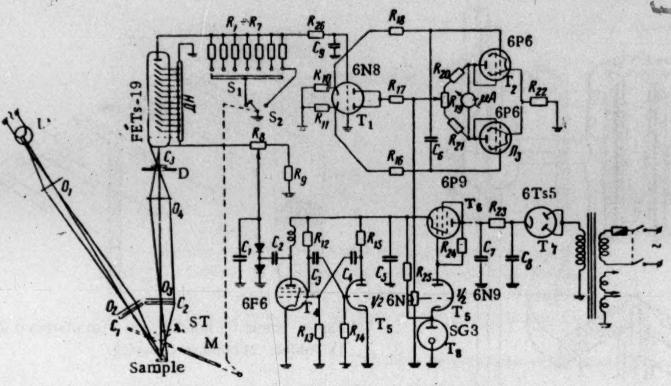

Fig. 5. Optical-electric setup of the photometer.

Among the problems confronting us was the development of a luminescent photocolorimeter which would have the requisite sensitivity and accuracy, and would be sufficiently compact and simple.

The apparatus, which was based on a one-lens optical system with direct reading, has a casette which is suitable for working with both disc samples and with beads.

The source of the exciting radiation is an incandescent lamp with a power of 50 watts fed from a ferro-resonance voltage stabilizer. The compactness of the incandescent body combined with the optical system, make possible the efficient use of the light flow of the lamp, and, when a sensitive photoelectric setup is available, it can be used instead of the mercury quartz source which is less convenient to operate.

The image of lens O_1 is projected by lens O_2 (Fig. 5) onto the surface of the sample in the form of a uniformly illuminated circle. An ultraviolet filter C_1 is set up in the ray path. The image of the luminescing sample is projected by lens O_3 onto the surface of the diaphragm D which holds back the light of the luminescence from the contaminated surface of the casette. The uniformly illuminated image of lens O_3 is projected onto the surface of the photocathode surface by lens O_4.

The yellow-green filter C_2 and the light-blue filter C_3 absorb the interfering primary radiation passing through filter C_1 and scattered by the sample surface. The photocurrent of the multiplier is amplified by the tubes T_1, T_2, and T_3 and causes a deflection of the microammeter needle which is proportional to the intensity of the radiation from the sample. The sensitivity range is selected by the switch S_1 in the grid circuit of the emplifier.

The apparatus is designed so that checking can be carried out by correcting the sensitivity by means of a special luminescing standard ST which can be inserted into the optical system instead of the sample being measured by means of a mirror M connected firmly with the switch S_2. Such a design enables one to correct the sensitivity of the photometer before each measurement for any position of the switch S_1. The sensitivity is controlled by means of a potentiometer R_8 which alters the voltage of the supply FÉU. The high voltage for feeding the photomultiplier is developed by an impulse source on the tube T_4 and by the left half of the double triode T_5 stabilized by an electronic stabilizer on tubes T_6, T_5, and T_8.

Variations in the circuit voltage and changes in the parameters of the scheme are not reflected in the measurements, thanks to the use of the internal standard.

When the needle of the apparatus, with the illuminator switched off, is set on zero, then the reading given by the illuminated, hardened, but still-hot disc, — i.e., known not to luminesce — does not exceed 1 mm, while the reading from the cold "blank" disc prepared from a reagent chosen on the basis that it has the least luminescence

TABLE 1

Determination of Uranium in Ores by the Method of Additions

Specified U content of the ore, %	U found, %		Mean, %	Mean error (relative), %
0,028	0,022	0,024	0,026	— 7,2
	0,024	0,031		
	0,025	0,025		
0,016	0,016	0,015	0,014	—12,5
	0,014	0,013		
0,072	0,069	0,078	0,072	0
	0,068	0,077		
	0,072	0,065		
0,102	0,089	0,093	0,094	— 7,8
	0,093	0,088		
	0,108	0,090		
0,059	0,058	0,066	0,059	0
	0,058	—		
	0,051	0,062		
0,082	0,082	0,091	0,082	0
	0,086	—		
	0,081	0,072		
0,070	0,076	0,080	0,079	+12,8
	0,090	0,079		
	0,072	—		

is 8 mm. The residual luminescence of this disc is equivalent to a uranium concentration of the melt of 0.004 μg/g. Over the maximum sensitivity range, the full scale deflection corresponds to a concentration of 0.08 μg/g.

The overlap coefficients for the ranges is equal to three. Readings for a disc which has a uniform uranium distribution (4.8 μg/g) and has been stored in a desiccator are reproducible over a period of a week with an accuracy of ± 1.5%.

Determination of Uranium without Preliminary Purification of the Samples

It is known that in the presence of a large part of impurities, the linear relationship between the uranium concentration of a melt and the intensity of the luminescence is maintained. The proportionality coefficient depends on the composition of the solution and the concentration of impurities, but is almost independent of the uranium concentration [4].

The relation between the luminescence intensity and the uranium concentration of the melt can be expressed by the equation

$$n_x = K_{pc}\,(x + \varphi)$$

where n_x is the reading given by a sample activated by the amount of uranium it is required to determine; $\underline{x}$ is the sought-for weight of uranium in the sample; φ is the amount of uranium equivalent to the radiation given by a "blank" sample, and K_{pc} is the proportionality coefficient in the presence of impurities.

It is assumed that the impurities which are present affect the luminescence of the "blank" sample in the same way as they affect the luminescence of the sample containing uranium. On adding to a sample, an additional, known amount of uranium, the luminescence intensity increases: $n_{x+a} = K_{pc}\,(x + \varphi + a)$, the proportionality coefficient being the same, since the composition and the amount of impurities remains the same as before. From these two equations we find that

$$x = \frac{n_x \cdot a}{n_{x+a} - n_x} - \varphi.$$

TABLE 2

Determination of Uranium in Ores using Preliminary Dilution

Specified U content of the ores, %	Final vol. when an ore sample of 100 mg was used, ml	U found, %		Mean, %
0,031	50	0,028	0,029	0,029
		0,038	0,022	
		0,021	0,015	
0,016	50	0,015	—	0,015
		0,011	0,015	
0,070	250	0,075	0,067	
		0,055	0,072	0,067
0,059	150	0,067	0,057	0,062
		0,066	0,059	
		0,074	0,074	0,072
0,072	200	0,076	0,066	

Table 1 contains results obtained during the determination of uranium by such a technique in several samples from different deposits.

The luminescing discs were prepared in an electric oven with a platinum case from a solution obtained directly after decomposition of the ore. In parallel, samples were prepared, the uranium in which had been introduced simultaneously from the test solution and from a solution with a known uranium concentration.

It should be noted that there is a considerably greater scatter between the radiation intensities of individual samples than in the case of samples prepared from pure solutions of uranyl salts. This can be partly explained as follows. With increasing concentration of the extinguisher, the luminescence intensity drops, and approximates to some limiting value corresponding to saturation of the melt with dissolved impurity. Excess of the impurities deposits on the bottom of the basin and does not interfere with the photometric determination of the upper, radiating layers of the sample. With increasing amounts of undissolved residue, the latter penetrates into the upper layers of the sample, causing further weakening of the light beam. Uneven distribution of flocs of deposits in the melt cause a scatter in the readings of the apparatus. In order to achieve the highest accuracy by the method of additions, it is useful to couple the determination with a simple partial purification, and, if possible, with preliminary dilution of the test solution.

When the proportionality coefficient between the illumination and the concentration is equal to K_o for samples prepared from pure solutions of uranyl salts, while for samples containing impurities, this coefficient is K_{pc}, then, on diluting the solution, the ratio K_o/K_{pc} tends to unity. Thus by suitable dilution of the test solution, it is possible to decrease, or even to exclude the influence of the impurities, and to carry out a determination without preliminary purification.

Table 2 contains results for the determination of uranium in ores, in which dilution without preliminary removal of interfering elements was used. The samples were prepared in the form of beads.

SUMMARY

An electric furnace with a platinum case is suggested for preparing luminescent samples with increased accuracy. The reproducibility of luminescent discs prepared from a fluoride-carbonate mixture and a pure solution of a uranyl salt, amounts to ± 2% on the average.

A tube fitted with a piston is suggested for measuring out (dosing) the powder. The dosage accuracy is ± 1.5%.

An apparatus is suggested for granulating the melts. The granules are of uniform composition and possess high mechanical stability. The weight of the granules is 110 mg and can be reproduced with an accuracy of ± 1%.

An improved, express variant of the method of preparing samples in the form of drops (beads) is suggested. The reproducibility of the luminescence of beads prepared from sodium fluoride and a pure solution of a uranyl salt is equal to 6-7% on an average.

A design has been developed for a photoelectric apparatus for measuring the luminescence intensity of discs, beads, and powders. Full scale deflection of the needle (150 mm) at the maximum sensitivity range of the apparatus corresponds to a uranium concentration in a disc of 0.08 μg/g. Readings for samples with a uniform distribution of uranium are reproduced with an accuracy of ± 1.5%.

Methods for determining uranium without preliminary purification have been tested on standard ores.

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MOLYBDENOMETRY

COMMUNICATION 2. TITRATION OF SEXIVALENT MOLYBDENUM BY MEANS OF A SOLUTION OF A TRIVALENT MOLYBDENUM SALT*

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Methods were described previously for the preparation, storage, and standardization of solutions of trivalent molybdenum [1]. It was shown that, under certain conditions, a fully stable solution can be obtained. In the work described here a study was made of the possibility of determining sexivalent molybdenum quantitatively in the presence of a number of elements by titration with a solution of a trivalent molybdenum salt. The values of the potentials of Mo^{V}/Mo^{III} and Mo^{VI}/Mo^{V} have been measured by a number of authors [2-4]. There is an incidental reference in the literature [5] that during titration of sexivalent molybdenum with a solution of trivalent molybdenum, at a certain point there is a fairly clearly defined potential jump on the platinum electrode. The reduction of Mo^{VI} by a solution of a Mo^{III} salt to give Mo^{V} in a hydrochloric acid solution has already been studied [6].

EXPERIMENTAL

Standard solutions of trivalent molybdenum salts were prepared and stored as described before [1].

Ammonium molybdate solutions were prepared by dissolving the chemically pure salt in water; the solutions were standardized by weighing molybdenum as $PbMoO_4$.

The apparatus was the same as that described previously. A saturated calomel electrode was used as the reference electrode. A platinum disc was used as the indicator electrode.

Results of a Study of the Reduction of Sexivalent Molybdenum by a Trivalent Molybdenum Solution

Trivalent molybdenum under certain conditions should reduce sexivalent molybdenum to quinquevalent molybdenum, or less likely, to the quadrivalent state. There are many published references [7] to the existence of quadrivalent molybdenum. At the same time, during potentiometric reductometric titrations, no potential jumps are observed corresponding to the completion of the reduction of molybdenum to the quadrivalent state. Accordingly, the first thing we had to clarify was how trivalent molybdenum reacts with sexivalent molybdenum under various conditions.

During a study of the quantitative proportions during the interaction of sexi- and trivalent molybdenum, 70 ml of 8-10 N HCl was added to a known volume of a standard ammonium molybdate solution, atmospheric

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*For Communication 1, see Zhur. Anal. Khim. 14, 668 (1959).

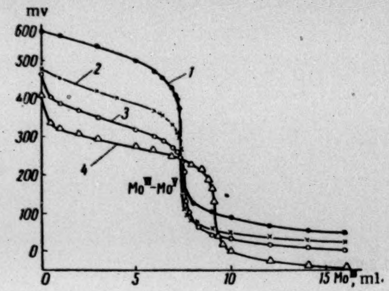

Fig. 1. Titration curves of sexivalent molybdenum with a trivalent molybdenum salt solution in hydrochloric acid media. In each case 5.0 ml of 0.1 M ammonium molybdate (0.04795 g Mo) and 70 ml of hydrochloric acid of varying concentrations were taken. $T_{Mo^{III}/Mo^{IV}} = 0.006448$. Capacity of titration vessel 150 ml. 1) HCl (sp. gr. 1.19) at 55-60°; 2) HCl (2 : 1) at 55-60°; 3) HCl (1 : 1) at 70-75°; 4) HCl (1 : 2) at 70-75°. The potential jump of the platinum electrode on curves 1, 2, 3, and 4 is found, respectively, on addition of 7.6, 7.5, 7.7, and 9.2 ml of trivalent molybdenum solution.

oxygen was removed from the solution by passing carbon dioxide through it for 20-25 minutes, and the solution then titrated with trivalent molybdenum solution at 55-65° using a platinum indicator electrode. The trivalent molybdenum solution was standardized against potassium dichromate using Mohr's salt.

Only one large potential jump was observed on the titration curves; this corresponded, as the results given in Table 1 show, to completion of the reduction of sexivalent molybdenum to the quinquevalent state.

Thus, in a hydrochloric acid medium, one mole of trivalent molybdenum reduces two moles of molybdate exactly. The course of the reaction can be expressed by the equation:

$$2MoO_4^{2} + Mo^{III} + 16H^+ = 2Mo^V + 8H_2O.$$

Since the reaction proceeds strictly stoichiometrically and rapidly under certain conditions, it can be used as the basis of a potentiometric method for determining molybdenum. It is evident from the equation that the gram equivalent of molybdate is equal to its molecular weight, while the gram equivalent of trivalent molybdenum is equal to half of its atomic weight.

The effect of the hydrochloric acid concentration in the solution being titrated on the titration curve of sexivalent molybdenum with trivalent molybdenum solution is evident from Fig. 1. When the initial hydrochloric acid in the solution being titrated is greater than 8 N, reduction of sexivalent molybdenum with a trivalent molybdenum solution is strictly stoichiometric. When the initial hydrochloric acid concentration is < 6N, a larger amount of trivalent molybdenum is used for titrating the sexivalent molybdenum than is theoretically necessary. Decreasing the hydrochloric acid concentration of the solution being titrated leads to a decrease in the potential jump, and, at the same time, slows down the rate of reduction. It must be pointed out that during titration of sexivalent molybdenum with a solution of trivalent molybdenum in hydrochloric acid (1 : 1), or in a medium of concentrated HCl, on addition of large amounts of KCl, $CaCl_2 \cdot 6H_2O$, or $MgCl_2$ (Fig. 2), the potential jump occurs at the equivalence point, but addition of KCl or $MgCl_2$ does not have any appreciable effect

TABLE 1

Titration of Sexivalent Molybdenum with Trivalent Molybdenum in Hydrochloric Acid Media

Ammonium molybdate taken			Amt. of Mo^{III} used up to get the potential jump			Molar ratio Mo^{VI}/Mo^{III}
solution, ml	$T_{Mo^{VI}}$	mM	solution, ml	$T_{Mo^{III}/Mo^{III-V}}$	Mo^{III} mM	
10,00	0,009590	0,9995	11,96	0,004014	0,5003	1,998
10,00	0,009590	0,9995	11,41	0,004195	0,4989	2,003
10,00	0,009590	0,9995	12,63	0,003800	0,5002	1,998
20,00	0,004808*	1,002	12,02	0,003894	0,5003	2,003
10,00	0,009590	0,9995	12,0	0,003894	0,4995	2,001

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* The molybdenum content was determined by weighing it in the form of molybdenum 8-hydroxyquinolate.

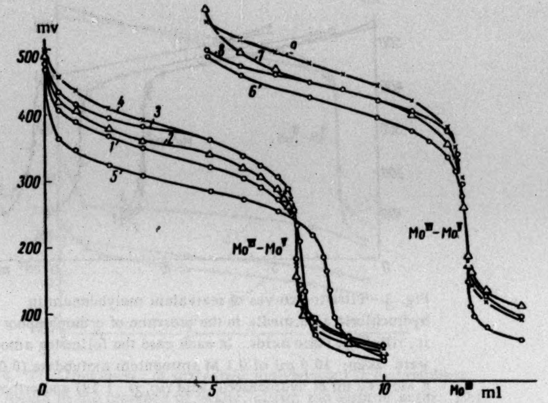

Fig. 2. Titration curves of sexivalent molybdenum in hydrochloric acid media in the presence of potassium chloride, calcium chloride or magnesium chloride. In each case 5.0 ml of 0.1 M ammonium molybdate (0.04795 g Mo) was taken, together with 70 ml of hydrochloric acid of varying concentration and KCl to the saturation point, 25 g $CaCl_2 \cdot 6H_2O$ or 20 g $MgCl_2$. Temperature 70-75°. Capacity of titration vessel 150 ml. 1) HCl, 1 : 1; 2) HCl 1 : 1, KCl to saturation; 3) HCl 1 : 1, 25 g $CaCl_2 \cdot 6H_2O$; 4) HCl 1 : 1, 20 g $MgCl_2$; 5) HCl 1 : 2, KCl to saturation; 6) HCl 2 : 1; 7) HCl 2 : 1, KCl to saturation; 8) HCl 2 : 1, 25 g $CaCl_2 \cdot 6H_2O$; 9) HCl 2 : 1, 20 g $MgCl_2$. The potential jump of the platinum electrode on curve 5 is located at 8.6 ml of Mo^{III} solution, in the remaining curves it is found at 7.5 ml of Mo^{III} solution.

on the value of the potential jump and the reaction rate. When more dilute hydrochloric acid (1 : 2) is used, addition of KCl does not enhance the definition of the potential jump and does not increase the rate at which it is established, and the potential jump does not coincide with the equivalence point.

In Fig. 3 and 4 are shown the curves for the titration of sexivalent molybdenum with a trivalent molybdenum solution in a strongly hydrochloric acid medium (with a platinum indicator electrode) in the presence of orthophosphoric or boric acid, silicic acid, tartaric, citric, or oxalic acid.

Small amounts of orthophosphoric or boric acid hardly interfere at all with the determination of molybdenum. In the presence of large amounts of orthophosphoric or boric acid the potential jump occurs somewhat later than the equivalence point, however, the error that is observed can be disregarded in many cases. Silicic acid shows hardly any effect on the titration process. Tartaric, citric, and oxalic acids have hardly any effect on the position and the value of the potential jump during the titration of molybdenum in a strongly hydrochloric acid medium. In the absence of hydrochloric acid, when the solution contains molybdate alone and only one of the acids indicated, no potential jump is observed.

Of some interest is the replacement of the platinum electrode by electrodes made of other more readily available materials during the potentiometric titration of sexivalent molybdenum with a trivalent molybdenum solution in hydrochloric acid media.

It is clear from Fig. 5 that a clearly defined, large potential jump is observed at an initial HCl concentration of 2 : 1 on titrating with platinum, graphite, and amalgamated platinum electrodes; when a tantalum and tungsten electrodes are used only a small potential jump is observed. Accordingly, tantalum and tungsten electrodes cannot be recommended for the titration, in practice, of sexivalent molybdenum with a trivalent molybdenum solution.

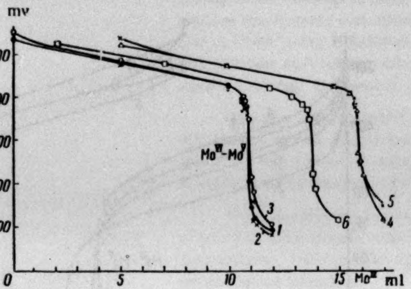

Fig. 3. Titration curves of sexivalent molybdenum in hydrochloric acid media in the presence of orthophosphoric, silicic or boric acids. In each case the following amounts were taken: 10.0 ml of 0.1 M ammonium molybdate (0.09535 g Mo), 60 ml of hydrochloric acid (sp. gr. 1.19) and orthophosphoric, silicic, or boric acids. Temperature 60-65°. Capacity of titration vessel 150 ml. 1) HCl; 2) HCl, 1 ml of orthophosphoric acid (sp. gr. 1.7); 3) HCl, 10 ml of orthophosphoric acid (sp.gr. 1.7); 4) HCl, 3 g boric acid; 5) HCl, 5 g boric acid; 6) HCl, 1 g sodium silicate. The potential jumps of the platinum electrode on curves 1, 2, 3, 4, and 5 are located, respectively, at points corresponding to the addition of 11.01, 11.02, 11.06, 11.06, 11.03, and 11.05 ml of Mo^{III} solution ($T_{Mo^{III}/Mo^{VI}}$ = = 0.008676); on curve 6 it is found at 11.92 ml of Mo^{III} solution ($T_{Mo^{III}/Mo^{VI}}$ = 0.008013).

It is possible that tungsten and tantalum electrodes behave partly as oxide-hydrogen electrodes under titration conditions used.

Tungsten does not interfere with the titration of sexivalent molybdenum with a trivalent molybdenum solution in a concentrated hydrochloric acid medium under certain conditions. The hydrochloric acid concentration should be such that all the tungsten is in solution. As the amount of tungsten increases, the positive experimental error obtained increases (Table 2). When tungsten is kept in solution by addition of oxalic acid, while a high concentration of hydrochloric acid is maintained, satisfactory results can be obtained for molybdenum in the presence of relatively large amounts of tungsten (Table 3). When, during titration of molybdenum, a turbidity develops on account of tungstic acid, inaccurate results are obtained for molybdenum.

The following procedure is adopted for the determination of molybdenum in the presence of tungsten. To the weakly acid solution of sodium molybdate and tungstate is added a sufficient amount of oxalic acid and the solution evaporated to the appearance of the first crystals on the walls of the vessel. To the solution is then added 60 ml of concentrated hydrochloric acid, while the solution remains completely clear all the time; all the tungsten is found in solution in the form of the oxalate complex. If the solution, after addition of oxalic acid, is not evaporated, then on subsequent addition of 60 ml of concentrated hydrochloric acid, a turbidity of tungstic acid is formed which then dissolves; however, incorrect results are obtained for molybdenum. The hydrochloric acid oxalate solution obtained is titrated with a solution of a trivalent molybdenum salt in a CO_2 atmosphere at 60-65°. A large potential jump is observed at the end point. When such a technique is used, satisfactory results are obtained for molybdenum, even in the presence of relatively large amounts of tungsten (Table 3). The error for molybdenum decreases with increasing amounts of oxalic acid used for keeping the tungsten in solution in a concentrated hydrochloric acid medium.

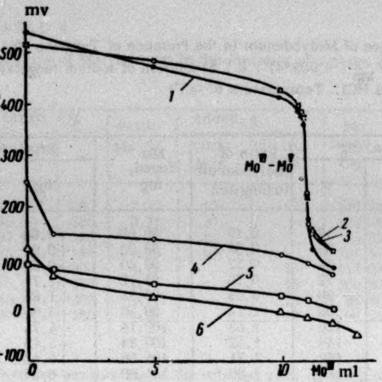

Fig. 4. Titration curves of sexivalent molybdenum in hydrochloric acid media in the presence of oxalic, citric, and tartaric acids. 10.0 ml of 0.1 M ammonium molybdate (0.09535 g Mo) was taken in each case together with hydrochloric acid, oxalic, citric, or tartaric acid. Temperature 60-65°. Capacity of titration vessel 150 ml. $T_{Mo^{III}/Mo^{VI}}$ = 0.008676). 1) 60 ml HCl (sp. gr. 1.19), 15 g oxalic acid; 2) 60 ml HCl (sp.gr. 1.19), 15 g citric acid; 3) 60 ml HCl (sp.gr. 1.19), 10 g tartaric acid; 4) 60 ml of a saturated solution of oxalic acid in the absence of hydrochloric acid; 5) 60 ml of a saturated solution of citric acid in the absence of HCl; 6) 60 ml of a saturated solution of tartaric acid in the absence of HCl. The potential jump of the platinum electrode on curves 1, 2, and 3 is found at a point corresponding to the addition of 11.01 ml of Mo^{III} solution, while on curves 4, 5, and 6 no potential jump is observed at all.

When, instead of 60 ml of concentrated hydrochloric acid (when 30 g of oxalic acid is used), 60 ml of HCl 1 : 1, HCl 1 : 2, or HCl 1 : 3 is used, high results are obtained for molybdenum, the results being higher the lower the initial hydrochloric acid concentration (instead of 12.80 ml of Mo^{III} solution, 13.04, 13.40, and 13.80 ml of Mo^{III} solution was used, respectively). Under these conditions only a small potential jump was observed. Tests showed that tartaric and citric acids were not effective in keeping the tungsten in solution in concentrated hydrochloric acid (to an aqueous solution of molybdate and tungstate was added excess of tartaric or citric acid, the solution was then evaporated to the appearance of crystals, and concentrated hydrochloric acid added). In these cases unsatisfactory results were obtained during titration of molybdenum (Table 4).

Nickel, cobalt, and cadmium have almost no effect on the titration results of sexivalent molybdenum in a concentrated hydrochloric acid medium (in the absence of oxalic acid). Thus, 11.01 ml of Mo^{III} solution was expended in titrating 10.0 ml of 0.1 M molybdate solution (T_{Mo} = 0.009535), while for titrating the same amount of molybdate to which had been added 5 ml of 0.1 M solutions of nickel, cobalt, or cadmium chloride, 11.15, 11.09 and 11.16 ml of Mo^{III} solution was used ($T_{Mo^{III}/Mo^{VI}}$ = 0.008676). Titanium, aluminum, magnesium, and bismuth have hardly any effect on the titration results for molybdenum (5.0 ml of the 0.1 M solutions of the salt of each element was added). Permanganate and dichromate are reduced at 65-80° in a strongly hydrochloric acid medium to the lower valence states with liberation of free chlorine which is removed by passing CO_2 through the solutions, as a result of this, correct results are obtained during titration of sexivalent molybdenum.

Quinquevalent vanadium is partially reduced at 65-80° by concentrated hydrochloric acid to the quadrivalent state. During subsequent titration with a trivalent molybdenum solution, two potential jumps are observed, the position of which does not permit calculation of the amount of molybdenum.

TABLE 2

Determination of Molybdenum in the Presence of Tungsten (0.1 M ammonium molybdate T_{Mo} = 0.009541 + 0.1 M solution of sodium tungstate + 60 ml of concentrated HCl. Temperature 60-65°)

Taken, mg		Ratio of molybdenum to tungsten	Mo found, mg	Exptl. error	
Mo	W			mg	%
95,41	18	0,19	96,08	+0,68	0,70
95,41	36	0,38	96,32	+0,91	0,95
95,41	54	0,57	96,40	+0,99	1,04
95,41	72	0,76	97,12	+1,71	1,79
95,41	90	0,95	97,24	+1,83	1,92
95,41	108	1,14	99,50	+4,09	4,29
95,41	126	1,33	100,16	+4,75	4,98
95,41	144	1,52	100,84	+5,43	5,69
95,41	162	1,71	101,56	+6,15	6,45
95,41	180	1,90	101,80	+6,39	6,70
47,70	90	1,89	48,50	+0,80	1,67
47,70	108	2,26	50,18	+2,38	4,99
47,70	126	2,64	51,98	+4,28	8,97
47,70	144	3,02	52,20	+4,50	9,43
47,70	162	3,35	53,16	+5,46	11,45
47,70	180	3,77	54,80	+7,10	14,88

TABLE 3

Determination of Molybdenum in the Presence of Tungsten

Taken, mg		Amount of $H_2C_2O_4$ used to keep tungsten in sol.	Ratio Mo : W	Mo found, mg	Exptl. error	
Mo	W				mg	%
95,41	360	20	3,77	95,48	+0,07	+0,07
95,41	540	10	5,66	99,06	+3,65	+3,82
95,41	540	20	5,66	95,70	+0,29	+0,30
95,41	540	30	5,66	95,48	+0,07	+0,07
95,41	900	40	9,43	95,54	+0,13	+0,13
95,41	1080	50	11,32	95,11	—0,30	—0,31
95,41	1260	60	13,20	95,54	+0,13	+0,13
47,71	720	30	15	48,02	+0,31	+0,65
47,71	1440	80	30,18	47,88	+0,17	+0,35
143,12	720	40	5,03	142,65	+0,47	—0,32
190,82	720	40	3,77	190,32	—0,5	—0,26
95,41	720	30	7,54	95,48	+0,07	+0,07
95,41	360	20	3,77	104,43	+9,02	+9,45•

• After adding oxalic acid to the solution of molybdate and tungstate the solution was not evaporated; accordingly, unsatisfactory results were obtained for molybdenum.

Sexivalent uranium is reduced by trivalent molybdenum and interferes with titration of sexivalent molybdenum.

Tellurium• does not interfere with molybdenum determination. During titration in a concentrated hydrochloric acid medium the molybdenum is reduced first, followed by the tellurium (Table 5). Two potential jumps are observed on the titration curves.

• The tellurium solution was prepared as follows: 0.5 g of tellurium metal was dissolved in nitric acid; after the tellurium had dissolved the solution was evaporated with H_2SO_4 to the appearance of SO_3; then the solution was finally made up to 250 ml with water.

TABLE 4

Titration of Molybdenum in the Presence of a Large Amount of Tungsten

Taken, mg		Ratio Mo : W	Added, g		Mo found, mg	Exptl. error	
Mo	W		citric acid	tartaric acid		mg	%
95,90*	360	3,77	15		106,48	+10,58	11,03
95,90	360	3,77	20		102,47	+ 6,57	6,85
95,90	360	3,77	15		95,65	— 0,25	0,26
95,90	180	1,88	10		101,17	+ 5,27	5,49
95,90*	360	3,77		15	113,03	+17,13	17,86
95,90	360	3,77		15	106,37	+10,47	10,92
95,90	360	3,77		20	97,76	+ 1,86	1,94
95,90	180	1,88		10	99,95	+ 4,05	4,22

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* Without evaporation of the solution after addition of citric and tartaric acid.

TABLE 5

Titration of Molybdenum in the Presence of Tellurium. 10.0 ml of 0.1 M Ammonium Molybdate (0.09590 g Mo), 60 ml of Concentrated Hydrochloric Acid, and 10 ml of Tellurium Solution were Taken; $T_{Mo^{III}/Mo^{VI}}$ = 0.008000; Temperature 65°

10 ml of $(NH_4)_2MoO_4$ in the absence of Te			10 ml of H_2TeO_4 in the absence of Mo			10 ml of $(NH_4)_2MoO_4$ and 10 ml of H_2TeO_4		
Mo^{III}, ml	mv	ΔE/ΔV	Mo^{III}, ml	mv	ΔE/ΔV	Mo^{III}, ml	mv	ΔE/ΔV
0	555		0	230		0	576	
5	495		0,1	195		1	535	
10	440		0,2	184		15	475	
11	421		0,5	171		10	400	
11,5	400		1,0	175		11	377	
11,7	383		1,5	171	8	11,5	353	
11,8	371	120	2,0	136	70	11,8	320	110
11,9	358	130	2,1	41	1150	11,9	300	200
12,0	211	1470	2,2	2	390	12,0	253	470
12,1	159	520	2,3	15	270	12,1	225	280
12,2	135	240	2,5	—20		12,2	211	
12,5	100		3,0	—25		12,5	208	
13,0	77		3,5	—30		13,0	200	
14,0	60					13,2	175	125
						13,3	90	350
						13,4	75	150
						14,0	54	
						15,0	40	

The amount of Mo^{III} solution used up to the first potential jump corresponds to the molybdenum content. The amount of Mo^{III} solution used up between the first and second jump should correspond to the tellurium content, but it differs from the amount of Mo^{III} solution used up for titration of tellurium in the absence of ammonium molybdate.

During titration of molybdenum and selenium in a concentrated hydrochloric acid medium, one potential jump is observed, this corresponds to the co-reduction of these elements (Fig. 6).

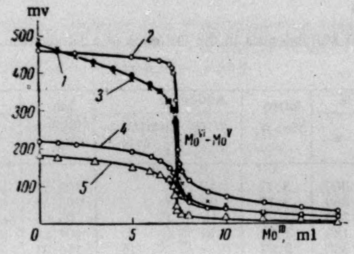

Fig. 5. Titration curves for sexivalent molybdenum with various indicator electrodes. 5.0 ml of 0.1 M ammonium molybdate (0.04795 g Mo) and 70 ml of hydrochloric acid (2 : 1) were used. Temperature 65° ($T_{Mo^{III}/Mo^{VI}}$ = 0.006492). Titration curves with the electrodes: 1) Platinum; 2) amalgamated platinum; 3) graphite; 4) tungsten; 5) tantalum. 7.4 ml of Mo^{III} solution was used with all the electrodes.

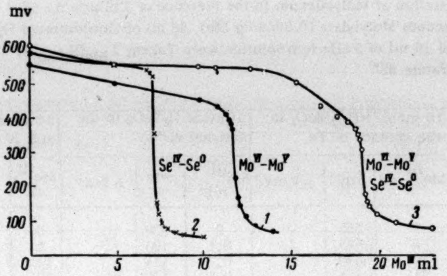

Fig. 6. Titration curves of sexivalent molybdenum and quadrivalent tellurium in their mixtures in hydrochloric acid media. 10.0 ml of 0.1 M ammonium molybdate (0.09590 g Mo), 5.0 ml of H_2SeO_3, and 60 ml of HCl sp.gr. 1.19 were taken. Temperature 60-65°. ($T_{Mo^{III}/Mo^{VI}}$ = 0.008000). Capacity of titration vessel 150 ml. 1) Titration of ammonium molybdate; 2) titration of Se^{IV}; 3) titration of a mixture of molybdenum and selenium. The potential jump of the platinum electrode on curves 1, 2, and 3 was found at points corresponding to the addition of 12.0, 7.4, and 19.4 ml of trivalent molybdenum solution, respectively The selenium solution was prepared as follows: 1 g of selenium metal was dissolved in nitric acid, after it had dissolved, the solution was evaporated with H_2SO_4 to the appearance of SO_3 when its volume was made up to 250 ml with water.

Divalent copper and trivalent iron are reduced together with sexivalent molybdenum in a concentrated hydrochloric acid medium. The potential jump corresponds to the sum of divalent copper and sexivalent molybdenum or to the sum of trivalent iron and sexivalent molybdenum.

Sexivalent molybdenum and trivalent iron are titrated together in a medium of sulfuric or orthophosphoric acid of various concentrations, and also on addition of oxalic, tartaric, or citric acid to the hydrochloric acid solution. Thus it was not found possible to separate appreciably the potentials of the system Mo^{VI}/Mo^{III} and Fe^{III}/Fe^{II}.

SUMMARY

Reduction of sexivalent molybdenum has been studied with the aid of a trivalent molybdenum solution. Under certain conditions the reaction is strictly stoichiometric in accordance with the following equation:

$$2MoO_4^{2-} + Mo^{III} + 16H^+ = 3Mo^V + 8H_2O.$$

A study has been made of the behavior of a number of elements under the conditions used for titrating sexivalent molybdenum.

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DETERMINATION OF PALLADIUM WITH β-HYDROXY-α-NAPHTHOIC ALDEHYDE

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It was pointed out earlier [1] that solutions of palladium salts react in the cold with β-hydroxy-α-naphthoic aldehyde, without addition of ammonia or alkali, to form a complex compound with the composition: $C_{22}H_{14}O_4Pd$. Crystals of the complex have a characteristic form (fine needles) and differ from the other complex salts of this aldehyde. β-Hydroxy-α-naphthoic aldehyde has been suggested for the gravimetric determination of magnesium [2], copper [3], and beryllium [4]. Further study has shown that it is possible to precipitate palladium quantitatively by means of this hydroxyaldehyde from acid solutions (ph 2.5-3).

Dimethylglyoxime is most often used for the gravimetric determination of palladium [5-9]. From published data it is known that at pH < 5, dimethylglyoxime partially precipitates nickel. Palladium may also precipitate under the same conditions [10]. The optimum conditions for determination of nickel with dimethylglyoxime is at a pH of 5.5. Palladium dimethylglyoximate can be quantitatively precipitated from 2 N hydrochloric acid [11]. At the same time a method has been published in which small amounts of palladium is determined in the presence of considerably larger amounts of nickel by using dimethylglyoxime in an acid medium [7]. In addition to dimethyl dimethylglyoxime, the following reagents have been suggested for precipitating palladium α-furyldioxime and β-furyldioxime [12], salicaldoxime [6, 12], 4-methyl and 4-isopropyl-1,2-cyclohexanedioneoxime [13], α-benzoinoxime [12], methylbenzoyl glyoxime [6], diethyldithiophosphoric acid [14], etc. Recently a photometric method has been published for the determination of small amounts of palladium in the presence of overwhelming amounts of platinum, iron, cobalt, nickel, cooper, and other elements by means of 8-mercaptoquinoline [15].

Many of the gravimetric methods for determining palladium require preliminary separation of copper, lead cobalt, iron, nickel, and other metals. There is no need to do this when β-hydroxnaphthoic aldehyde is used. Experiments were carried out on pure salts, and then in the presence of copper, nickel, cobalt, lead, trivalent iron, cadmium, silver, and platinum.

Trivalent iron, as one would expect, reacts with the hydroxyaldehyde on account of the phenolic groups in the latter, forming thereby dark-brown solutions with a violet shade. Silver in the dark, in the cold, is not reduced by a 1-2% solution of the aldehyde in an acid medium. Determination of palladium in the presence of lead is of great practical importance [14].

For precipitation of palladium with β-hydroxy-α-naphthoic aldehyde small amounts of palladium are taken as in the case of precipitation with dimethylglyoxime, not more than 0.2 g in 200 ml of acid solution (pH 2.5-3).

EXPERIMENTAL

Preparation of Palladium Nitrate Solution. 0.2 g of palladium wire was dissolved on careful heating in nitric acid, sp.gr. 1.43. The solution was evaporated on a water bath to a volume of 1.5-2 ml, transferred to a standard flask and made up to 200 ml with water.

TABLE 1

Pd taken, mg	Dimethylglyoxime method		β -Dydroxy-α-naphthoic aldehyde method	
	Pd found, mg	absolute error, mg	Pd found, mg	absolute error, mg
5,00	4,94	—0,06	4,98	—0,02
5,00	5,10	+0,10	5,00	0,00
5,00	5,00	0,00	4,94	—0,06
5,00	4,87	—0,13	4,90	—0,10
3,00	2,90	—0,10	2,84	—0,16
3,00	2,92	—0,08	2,82	—0,18

β -Hydroxy- α-naphthoic aldehyde was synthesized from β -naphthol; it was distilled under vacuum and recrystallized from alcohol (m.p. 80-82°) [16].

Method of Determining Palladium. To 5 ml of the palladium nitrate solution of known concentration was added an equal volume of alcohol, and then 5 ml of a 1% alcoholic solution of the freshly prepared reagent. Rubbing with a glass rod for several minutes led to the crystallization of the complex palladium compound.

The yellow precipitate was allowed to stand for 20-25 minutes and then filtered through a No. 2 Schott filter, then washed with 50% alcohol and dried at 110°. The factor for converting to palladium is 0.2377.

It follows from the results given in Table 1 that the results of the determination of palladium by β -hydroxynaphthoic aldehyde and dimethylglyoxime agree among themselves; the experimental error is within permissible limits.

Determination of palladium in the presence of the following cations: Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Pb^{2+}, Ag^{+}, Cd^{2+}, Pt^{II}, was carried out in a similar fashion. To 5 ml of palladium nitrate solution of known concentration was added solutions of the nitrates of the elements indicated, taken separately, and in their mixtures. Alcohol was added to the solution until its concentration was 50% of the solution, the determination was then carried out as described above. Alcohol was added in the amount indicated to prevent precipitation of the reagent.

The amount of reagent used was increased when iron was present. When up to 100 mg of iron was present 10-15 ml of a 1% solution of the reagent was added, while when 125-150 mg of iron was present a correspondingly larger volume of reagent solution was used.

Deposition of the palladium complex was somewhat slower when iron was present, but on rubbing with a glass rod for 2-4 minutes, a precipitate started to separate out. After 25 minutes the precipitate was filtered off, washed three times with 50% alcohol, three to four times with water, and then again with 50% alcohol, it was finally dried at 110°.

In order to avoid too much dilution, which makes filtration difficult, fairly concentrated solutions of the added salts were used. Thus, the concentration of nickel, cobalt, cadmium, copper, and lead nitrates was 100 mg/ml, that of silver nitrate was 50 mg/ml, and that of iron 5-10 mg/ml. Platinum concentration was 2 mg/ml (in the form of $K_2[PtCl_4]$).

When silver or divalent platinum salts were added, the experiments were carried out in the dark, in the cold, in a nitric acid medium. Determination of palladium in the presence of platinum without preliminary separation of the latter may be of practical importance.

It follows from the results given in Table 2 that palladium can be determined gravimetrically in the presence of the cations indicated by precipitating it with β -hydroxy- α-naphthoic aldehyde. These cations, even in large amounts, do not interfere with palladium determination, but, in view of the fact that the time taken to filter the bulky precipitates thereby increases, we limited ourselves to the amounts given in Table 2.

TABLE 2

Pd taken, mg	Added, mg								Pd taken, mg	Absolute error, mg
	Cu^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}	Cd^{2+}	Fe^{3+}	Ag^{+}	Pt^{4+}		
4,98	—	5	5	5	5	—	—	—	4,89	—0,09
4,98	50	50	50	50	50	—	—	—	5,03	+0,05
4,98	50	50	50	50	50	—	—	—	4,90	—0,08
10,00	100	100	100	100	100	—	—	—	9,84	—0,16
4,00	100	100	100	100	50	125	50	—	4,10	+0,10
5,00	250	250	250	250	—	—	—	—	5,10	+0,10
5,00	—	—	—	—	—	—	—	12	4,90	—0,10
4,94	—	—	—	—	—	125	—	—	5,00	+0,06
5,00	500	500	500	250	—	50	100	—	5,00	0,00
5,00	250	250	250	250	250	100	—	12	5,03	+0,03
5,00	500	500	500	500	—	150	50	—	4,90	−0,10
4,94	—	—	—	—	—	50	200	—	5,06	+0,12
4,94	—	—	—	—	—	—	125	—	4,82	−0,12

Since Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Be^{2+} react with β-hydroxy-naphthoic aldehyde only in an alkaline medium [1], these elements should not hinder precipitation of palladium at a pH of 2.5-3. β-Hydroxy-naphthoic aldehyde precipitates nickel, cobalt, and copper at pH > 7. By varying the acidity during precipitation with the aldehyde, it is possible to determine palladium and one of the elements indicated on one aliquot. Work along these lines continues.

SUMMARY

A gravimetric method for the determination of palladium with β-hydroxy-α-naphthoic aldehyde in a nitric acid medium (ph 2.5-3) is suggested. Precipitation is carried out without heating.

The capacity of β-hydroxy-α-naphthoic aldehyde to react with certain cations at various pH values permits determination of palladium without its preliminary separation from copper, cobalt, nickel, and lead at ratios of palladium to metal of 1 : 100; from iron at a ratio of 1 : 15; from silver at a ratio of 1 : 20; and from platinum at a ratio of 1 : 2.

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A METHOD FOR THE DETERMINATION OF ABSOLUTE AMOUNTS OF IONIUM ($_{90}Th^{230}$)

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The isolation of the isotope $_{90}Th^{230}$ in a radiochemically pure form is of interest for the determination of the geological age of relatively young formations, for the study of the migration of ionium, and for other purposes. Recently the isotope $_{90}Th^{230}$ has been used for the synthetic preparation of the isotope $_{91}Pa^{231}$ The long half-life period of $_{90}Th^{230}$ [1] and the absence of β-radiation permits this isotope to be used as a α-radiation standard.

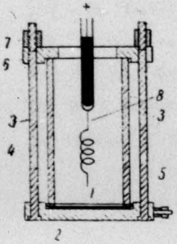
Since the discovery of ionium by Boltwood right up to the present time a large amount of work has been published [2] on improvements on the methods of isolating and measuring ionium. For the most complete separation of ionium from natural samples in a radiochemically pure state, it is usually separated together with a carrier. The extent of the separation of ionium can be established, as was done for the first time by Rona, on the basis of one of the thorium isotopes ($_{90}Th^{234}$, $_{90}Th^{228}$) added as an indicator. During measurement of the α-radiation of preparations of ionium with a carrier, calculation of absorption and self-absorption of α-radiation in the carrier layer presents difficulty One of the best methods of determining ionium in ores, suggested by I. E. Starik [3] permits the use of small aliquots of test material, and accordingly, small amounts of carrier. But even in these cases, self-absorption of the α-radiation occurs, and it is necessary to take measures to ensure that all the preparations are of the same thickness (0.1-0.2 mg/cm^2). It is known that during precipitation of cerium oxalates, the precipitate entrains from solution not only thorium isotopes, but appreciable amounts of the isotopes of bismuth, lead, and polonium, which should be removed.

The present article is devoted to a description of a method which ensures that ionium is obtained in a radiochemically pure state, and leads to its electrolytic deposition on the cathode in the form of an infinitely thin layer. We were particularly interested in the possibility of separating ionium during the electrolysis of cerium and foreign radioactive isotopes.

Electrolytic Separation of Thorium Isotopes. Information on the behavior of thorium isotopes during electrolysis is available in a number of papers [4]. In its chemical properties thorium belongs to the group of strongly electropositive elements. During electrolysis aqueous solutions of thorium salts are hydrolyzed at the cathode. The deposits of the basic thorium salts which are formed either adhere poorly or do not adhere at all to the electrode. When the amount of the hydrolyzed salt is very small, then, under certain conditions, it is possible to obtain deposits which do adhere (suitable for radiometry) to the electrode. Todt has shown that in order to obtain such deposits it is necessary to work at high current densities.

We have studied the conditions for the electrolytic separation of impulse amounts of thorium isotopes in the presence of uranium and thorium fission products, and in the presence of cerium salts.

Preliminary experiments which were carried out with the isotope $_{90}Th^{234}$ showed that the acidity of the medium has an essential influence on the extent of the separation of the thorium isotopes from solution. During



1) Platinum disc (cathode); 2) brass base; 3) vertical rods; 4) glass cylinder; 5) rubber ring; 6) plexiglass ring for pressing the cylinder onto the base; 7) screw; 8) platinum spiral (anode).

electrolysis, the hydroxyl ion concentration near the cathode increases. The mechanism of thorium precipitation is connected with the transference to the cathode of positively charged thorium ions which are deposited on the cathode in the form of a fine layer of thorium hydroxide. It is characteristic that in a sulfuric acid medium thorium isotopes are most completely separated at pH values close to 3.4. Presumably, this is connected with the formation on the cathode of a hydrate of thorium oxide, for which the pH value of a saturated solution is 3.4.

The solution to be electrolyzed was prepared as follows. Thorium isotopes were precipitated with 10-100 mg of cerium nitrate in the form of their oxalates from a hydrochloric acid medium (0.3 N HCl). The precipitates were allowed to stand overnight, they were then centrifuged, and washed, first with a small amount of oxalic acid solution, and then with distilled water, and finally dissolved in the minimum amount (1-2 ml) of nitric acid (1: 1); the solution was boiled and then evaporated almost to dryness with 1 ml of concentrated sulfuric acid to remove traces of nitric acid. In order to obtain the requisite acidity, and, at the same time, ensure that the electroconductivity of the solution is high enough, to the residue which had been evaporated with sulfuric acid was added 10 ml of a 10% solution of sulfuric acid, the solution was brought to the boil and then neutralized with ammonia. 10 ml of this solution and 2-3 ml of ethanol were taken for electrolysis. The solution to be electrolyzed was placed in the apparatus shown in the diagram

Platinum, stainless steel, gold-plated copper, etc., can be used as the cathode material. The purity and homogeneity of the surface is of great importance for the uniformity of the electrolytic deposit. Plates from platinum and stainless steel were polished beforehand, and immediately before use were boiled with alkali, washed with nitric acid, distilled water, and ether. The anode was a platinum wire coiled into a flat spiral which was placed parallel to the cathode at a distance of 3-4 mm from it. Electrolysis was carried out at a voltage of 3-4 volt applied to the terminals and a cathode current density of 180-220 ma/cm².

During electrolysis the temperature was kept within the range 70-80°. When the conditions indicated were used, 95-100% of the thorium isotopes were isolated on the cathode in the course of one hour in the form of an unweighable film. When electrolysis was complete, the cathode was rapidly withdrawn from the solution, rinsed with a mixture of alcohol and water (1 : 1) and calcined.

Experiments with $_{58}\mathrm{Ce}^{141}$ established that under the electrolysis conditions used, cerium present in the solution in amounts of 10-100 mg is hardly deposited at all on the cathode. It was also established that under the same conditions, not more than 4-5% of $_{83}\mathrm{Bi}^{210}$ (RaE) and 10% of $_{84}\mathrm{Po}^{210}$ (RaE) is deposited on the cathode, while on the anode more than 20% of $_{84}\mathrm{Po}^{210}$ and about 10% of $_{83}\mathrm{Bi}^{210}$ is deposited on the cathode, while on the anode more than 20% of $_{84}\mathrm{Po}^{210}$ and about 10% of $_{83}\mathrm{Bi}^{210}$ is deposited. Experiments with $_{91}\mathrm{Pa}^{233}$ showed that > 95% of protactinium remains in solution.

Thus it has been shown that it is possible, after preliminary separation of thorium isotopes together with cerium as the carrier, to carry out an electrolytic separation of the thorium isotopes on metal plates to give deposits which are suitable for radiometric measurements.

Preparation of Ionium Standards. Ionium standards were used for calibrating the apparatus. The original material used for preparing radiochemically pure ionium was a preparation obtained approximately 20 years ago; this was a preparation of the oxides of the rare earths which was enriched with ionium. Radiochemical purification of ionium from the accumulated radium and fission products consisted of the following steps: radium was removed from the original solution by a three-fold precipitation of barium-radium sulfates. Ionium was then successively twice precipitated with cerium fluoride and cerium oxalate. Cerium oxalate was dissolved in nitric acid, the solution was neutralized with ammonia, and the cerium hydroxide formed dissolved in 2 N hydrochloric acid. Completeness of removal of radium was controlled by means of the radon. Measurements of thoron and actinon demonstrated the absence of measurable amounts of the thorium isotopes of the thorium and actinium series. The radiochemical purity of the ionium preparation obtained was checked by a radiographic method [5]. The ionium content of the solution was determined from the radium accumulated and by calculating the absolute number of α-particles. For the α-count, five samples of ionium on backing of stainless steel were prepared electrolytically as described above from the freshly prepared solution. The rest of the solution was left for nine months in a quartz flask for the radium to accumulate. At the end of this period, three parallel samples were taken and the emanation measured on a DA setup which had been modified in our laboratory to measure small amounts [6].

The β-radiation of the ionium preparations separated by electrolysis was measured on a DA apparatus. Appropriate corrections were applied during calculation of the absolute amount of ionium in the original solution. The ionium content, expressed in terms of α-fissions per minute in 1 ml of solution, I_0, was calculated on the basis of the formula:

$$I_0 = \frac{I}{k_1 \eta k_2 k_3 v},$$

where I is the measured count rate, in cpm, k_1 is the correction for the resolving time of the apparatus (introduced on the basis of the curve relating resolving time to the α-count rate of the $_{84}\text{Po}^{210}$ preparations); η is the geometrical coefficient of the count, determined by means of uranium standards prepared by electrolysis from radiochemically pure uranium salts; k_2 is the ionium yield during electrolysis, this was determined on the basis of the yield of $_{90}\text{Th}^{234}$ isotope added to the solution; k_3 is the fraction of the total α-activity of the preparation which is attributable to the ionium α-radiation (this was determined radiographically); and v is the volume of the original solution used for electrolysis, in ml. The mean value found, for the ionium content, from a large number of measurements of the α-radiation of the five standards, was 4.59×10^{-6} g. The ionium content found on the basis of the radium accumulated was 5.13×10^{-6} g.* These results can be regarded as satisfactory.

Determination of Ionium in Ores. The suggested method was checked on samples of Yakhimov pitchblende, which according to the results of other determinations, was in equilibrium and was almost free from thorium.

First of all, the ionium content of the sample was evaluated from the total α-radiation of the powdered sample by the comparison method. The amount of sample taken, based on the activity of the material, was such that, assuming that 80% of the ionium was extracted and that all the corrections of the α-counter had been applied, it would give 50-500 cpm. The amount of the isotope $_{90}\text{Th}^{234}$ added in order to evaluate the degree of separation of ionium should be approximately ten times the β-radiation of the sample.

The aliquot of ore was dissolved on boiling in a mixture of 15 ml HNO_3 (1 : 1) and 5 ml of concentrated HCl. After the main bulk of the ore had dissolved, $_{90}\text{Th}^{234}$ was added to the solution. The insoluble residue, in the main silicic acid, was filtered off, and washed with hot 15-20% HCl. The activity of the residue was checked on a β-counter; usually, it was very small, approximately 0.3-0.5% of the activity introduced. In order to remove the soluble silicic acid, the filtrate was evaporated a few times with hydrochloric acid. 100 ml of 5% HCl was finally added and the silicic acid filtered off. The activity of the residue in the filtrate was also measured on a β-counter. It amounted to 0.5-1% of the initial. To the combined filtrates was added 30 mg of barium chloride and the barium precipitated with 10% sulfuric acid on heating. The precipitate was left to stand overnight; it was then filtered through a fine filter. The precipitate of barium and radium sulfates which had been thus filtered off was washed with 300 ml of 5% hydrochloric acid for removal of adsorbed thorium isotopes. To the filtrate plus wash liquors was added 20 mg of ferric chloride, the solution was neutralized with crystalline ammonium carbonate to the precipitation of a flocculent precipitate of ferric hydroxide which had adsorbed the thorium isotopes. The precipitate was heated for an hour on a water bath, it was then filtered off, washed with approximately 100 ml of ammonium carbonate solution for removal of traces of uranium, and was finally dissolved in the minimum volume of hydrochloric acid, and the acidity of the solution adjusted so as to be 0.3 N with respect to HCl. To the solution obtained was added a solution of cerium nitrate containing 100 mg of the salt, the thorium isotopes were precipitated with cerium oxalate, and the solution prepared for electrolysis as described above; the electrolysis was finally carried out. The α- and β-activities of the preparation were measured. From the β-radiation of $_{90}\mathrm{Th}^{234}$ the degree of separation of the thorium isotopes was calculated. As a result of the α-activity measurements, all the corrections necessary were applied, including the correction for the fractional content of the $_{90}\mathrm{Th}^{227}$ isotope equal to 0.046. In some cases the radiochemical purity of the ionium separated was checked radiographically by means of nuclear emulsions and the β - fission curve. For these purposes the thorium isotopes were isolated without additions of $_{90}\mathrm{Th}^{234}$. The normal curve for the β-fission of $_{90}\mathrm{Th}^{234}$ and $_{90}\mathrm{Th}^{231}$ testifies to the radiochemical purity of the isolated thorium isotopes. The ionium preparations did not contain more than 5% of other α-radioactive isotopes as impurity; this lies within the limits of our experimental errors.

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* The half-life period of ionium was taken to be 83,000 years for these calculations.

Calculation of the ionium content in the standard pitchblende showed that the amount present corresponds to the equilibrium amount with respect to uranium. The experimental error amounts to 5%.

Subsequently, the method was used for determining the ionium contents of uranium ores of varying origin. When the ratio of thorium to uranium does not exceed 0.1, then the share contributed by the α-radiation of $_{90}\mathrm{Th}^{234}$ and $_{90}\mathrm{Th}^{228}$ to the ionium radiation does not amount to more than 5%, which lies within the limits of experimental error. In the case of higher ratios of thorium to uranium, it is necessary to apply a correction to the results of the α-count; this can be done either radiographically or by means of a discriminator.

The method described permits one to separate 70-80% of the thorium isotopes and to take into account all the losses.

SUMMARY

A description is given of an electrolytic method of separating thorium isotopes without a carrier on metallic plates.

By means of this electrolytic method radiochemically pure ionium preparations are obtained which can be used as α-radiation standards.

A method is suggested for the separation and quantitative determination of ionium in natural samples.

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DETERMINATION OF FREE BORON IN BORON CARBIDE, BORON NITRIDE AND IN ALLOYS BASED ON THEM

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Determination of free boron in boron carbide and nitride is based on differences in the susceptibility to oxidation of free boron on the one hand, and of boron combined as the carbide or nitride, on the other. Moisson [1] pointed out long ago the possibility of dissolving boron in potassium permanganate. Kroll [2] developed a method for determining boron in amorphous boron, which was based on the oxidation of amorphous boron by a mixture of hydrogen peroxide and nitric acid. The capacity of boron to be oxidized by ceric sulfate has been used for developing a cerimetric method of determining boron in amorphous boron [3]. This method was used by Mikheeva et al. [4], for evaluating the quality of highly pure amorphous boron. In the method described [4] the cerimetric method was used for determining active boron in samples of boron of various degree of purity, in magnesium, aluminum, and calcium borides, and in boron carbide and nitride.

Boron, and magnesium, calcium, and aluminum borides are completely oxidized by potassium iodate and periodate, while boron nitride, boron carbide, and chromium and zirconium borides are not oxidized [5].

We have developed a method for determining free boron in boron nitride and carbide, and in alloys based on the latter compounds. In his discussion of the method for determining boron in amorphous boron, Kroll [3] points out that on treating amorphous boron with a mixture of hydrogen peroxide and nitric acid, the boron is not oxidized completely. The undecomposed residue consists of boron carbide and nitride, and the borides of several metals. We made use of this observation of Kroll for developing a method for determining free boron in the carbide and nitride.

We used a mixture of hydrogen peroxide (1 : 2) and nitric acid as an oxidizing agent for free boron.

The method for determining free boron in boron carbide and nitride was developed using samples of the following composition:

BN. Calculated 43.6% B and 56.4% N; found 41.84% B and 54.12% N
B_4C. Calculated 78.3% B and 21.7% C; found 76.9% B and 21.4% C.

In order to establish the behavior of boron carbide and nitride on treating them with mixtures of hydrogen peroxide and nitric acid, 0.3-0.5 or 1 g of the carbide or nitride, respectively, was ground to pass a 270 mesh sieve, and was then treated with a mixture of hydrogen peroxide and nitric acid in a 250 ml conical flask* fitted with a ground-glass reflux condenser. Boiling was carried out for 30, 45, 60, and 75 min. After the boiling the insoluble residue was filtered off. The residue of boron carbide or nitride was washed several times with cold water and 2-3 times with a 1% sodium hydroxide solution. After removal of carbon dioxide from the filtrate, its boron content was determined by titration with 0.1 N sodium hydroxide in the presence of mannite or invert sugar.

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* The flask was made from boron-free glass.

TABLE 1

First Treatment of Boron Carbide with the Hydrogen Peroxide-Nitric Acid Mixture

15 ml hydrogen peroxide (1 : 2) + 10 drops of HNO_3					45 ml hydrogen peroxide (1 : 2) + 10 drops of HNO_3				
aliquot, g	treatment time, min	0.1 N NaOH used, ml	0.1 N NaOH used up in the blank test, ml	free boron found, %	aliquot, g	treatment time, min	0.1 N NaOH used, ml	0.1 N NaOH used up in the blank test, ml	free boron found, %
0,5	30	1,7	0,2	0,33	1,0	30	3,8	0,7	0,32
0,5	45	1,8	0,3	0,34	1,0	45	3,7	0,7	0,32
0,5	60	1,9	0,3	0,34					
0,5	75	1,9	0,3	0,34					
0,5	90	1,9	0,3	0,34					
1,0	30	3,4	0,3	0,34					
1,0	45	3,45	0,3	0,35					

TABLE 2

Repeated Treatment of Boron Carbide with the Hydrogen Peroxide–Nitric Acid Mixture (0.5 g of sample, 45 ml $H_2O_2(1 : 2)$ + 10 drops of HNO_3)

Treatment time, min	0.1 N NaOH used, ml	0.1 N NaOH used in the blank test, ml	Free boron found, %
30	0.7	0.7	–
45	0.8	0.7	0.02
60	0.8	0.7	0.02

TABLE 3

Determination of Free Boron in Synthetic Mixtures of B_4C and Amorphous Boron (0.34% free boron was found, 0.500 g of B_4C contained 1.7 mg of free boron)

Boron added, mg	Boron that should be present, mg	Free boron found, mg	Relative error, %	Boron added, mg	Boron that should be present, mg	Free boron found, mg	Relative error, %
9,5	11,2	11,6	+3,4	16,25	17,95	18,4	+2,2
18,8	20,5	20,8	+1,17	26,43	28,13	27,70	–1,50
10,5	12,2	11,9	–2,4	49,0	50,7	50,26	–0,86
20,6	22,3	22,16	–0,85	50,1	50,8	51,02	+0,40

The washed, insoluble residue was dried at 110-120° to constant weight and again treated with the oxidizing mixture. Results obtained on treating boron carbide with a mixture of hydrogen peroxide and nitric acid are given in Tables 1 and 2.

On the basis of the results given in Tables 1 and 2, the following conclusions can be drawn. During treatment of boron carbide with a mixture of hydrogen peroxide and nitric acid, only the free boron is oxidized. Boron carbide is not oxidized at all under these conditions. A constant amount of boron, corresponding to the free boron content of the boron carbide, passes into solution, independently of the time for which the carbide is treated with the oxidizing mixture, and independently of the composition of the oxidizing mixture. When the boron carbide residue from the first treatment was given a second treatment with the oxidizing mixture no further amounts of boron passed into solution. Determination of boron in the filtrate demonstrated its absence. Boron is determined with an accuracy of 0.02%.

TABLE 4

Determination of Free Boron in Boron Nitride (first treatment with the oxidizing mixture)

15 ml hydrogen peroxide (1 : 2) + 10 drops HNO_3					30 ml hydrogen peroxide (1 : 2) + 10 drops HNO_3				
aliquot, g	treatment time, min	0.1 N NaOH used, ml	0.1 N NaOH used up in the blank test, ml	free boron found, %	aliquot, g	treatment time, min	0.1 N NaOH used, ml	0.1 N NaOH used up in the blank test, ml	free boron found, %
0,3	30	0,8	0,3	0,18	0,5	45	1,4	0,5	0,19
0,3	45	0,8	0,3	0,18	0,5	60	1,35	0,5	0,18
0,3	60	0,9	0,3	0,21	1,0	45	2,25	0,5	0,18
0,3	75	0,85	0,3	0,20	1,0	60	2,20	0,5	0,18

TABLE 5

Repeat Treatment of the Boron Nitride Residue with the Oxidizing Mixture (0.5 g aliquot. 30 ml of hydrogen peroxide (1 : 2) + 10 drops HNO_3 were taken)

Treatment time, min	0.1 N NaOH used, ml	0.1 N NaOH used up in the blank test, ml	Free boron found, %
45	0.5	0.5	0
60	0.45	0.5	0

In order to check on the suggested method for the determination of free boron in boron carbide, we made up and analyzed synthetic mixtures of amorphous boron and boron carbide in various proportions. These mixtures were treated with a solution of hydrogen peroxide and nitric acid as described above. Boron was determined in the filtrates by titration with invert sugar.

It follows from results obtained (Table 3) that free boron in boron carbide can be determined with reasonable accuracy by the method suggested.

During determination of free boron in boron nitride by treating the samples with the oxidizing mixture (a mixture of hydrogen peroxide (1 : 2) and nitric acid) the results shown in Table 4 were obtained.

According to these results the amount of boron which dissolved is always the same and corresponds to the free boron content of the boron nitride, the amount found being independent of the time for which the sample is treated with the oxidizing mixture and of the composition of the mixture. After the first treatment with the oxidizing mixture, the sample of boron nitride was filtered off, thoroughly washed with distilled water and the insoluble residue dried to constant weight. The boron nitride thus obtained, not containing free boron, was then given a second treatment with the oxidizing mixture. We wished to confirm by these experiments that boron nitride, not containing free boron is not decomposed by the oxidizing mixture. The results which we obtained are given in Table 5.

On the basis of these results it can be concluded that boron nitride is not oxidized by a mixture of hydrogen peroxide and nitric acid. The boron which dissolves during such a treatment corresponds to the free boron content of the boron nitride.

In order to check on the method for the determination of free boron in boron nitride, we analyzed alloys of of boron nitride and elemental boron. The free boron of these alloys was determined by the method described above. After decomposition of separate aliquots by fusion with sodium carbonate, the total boron and nitrogen (Kjeldahl) contents were determined.

TABLE 6

Determination of Free Boron in Boron Nitride-Boron Alloys

Sample No.	Nitrogen content (Kjeldahl), %	Total boron content, %	Free boron content, %	Combined boron calc. as a difference of total boron and free boron, %	Combined boron calc. on the basis of the nitrogen value, %
1	45,80	51,75	15,84	35,90	35,40
2	18,75	79,90	65,0	14,70	14,50
3	20,10	77,0	61,25	15,75	15,54
4	34,0	62,16	35,48	26,68	26,28

From the results on the determination of total and free boron the amount of combined boron in BN was determined. In addition, the amount of combined boron was calculated on the basis of the determination of the amount of nitrogen present. These results which were obtained for four alloys of boron nitride with elemental boron are given in Table 6.

EXPERIMENTAL PROCEDURE

0.1-1 g of boron carbide or boron nitride (depending on the free boron content) was treated in a 200-250 ml conical flask with a condenser with a ground-glass joint, with a mixture of 45-75 ml of hydrogen peroxide (1 : 2)* and 10 drops of nitric acid. The solution in the flask was slowly heated to the boil and then boiled for 40-45 minutes. For high amounts of free boron, an additional 3-5 ml of hydrogen peroxide was added. For free boron contents up to 5%, 15 ml of hydrogen peroxide (1 : 2) was sufficient. After the free boron had dissolved the solution was boiled for a further 10 minutes, it was then cooled and the condenser washed with water, the insoluble residue was filtered off (boron carbide or nitride). The residue was washed several times with water and 2-3 times with 1% sodium hydroxide solution. The weakly acid filtrate was boiled under reflux for removal of carbon dioxide. The solution was cooled, neutralized with 20% sodium hydroxide using methyl red as indicator, and 1-2 drops of hydrochloric acid (1 : 1) added, the solution was again neutralized with 0.1 N sodium hydroxide, the latter being added dropwise from a buret. To the neutral solution was added 10 ml of a 50% neutral solution of invert sugar, and the solution titrated using phenolphthalein as indicator until a permanent pink color was obtained. A blank was carried out through all the stages of the analysis.

$$B_{\text{free}} = \frac{(V - V_k)\cdot T\cdot 100}{d}\ \%,$$

where V is the volume of 0.1 N NaOH used in ml for titrating the solution of free boron; V_k is the volume of 0.1 N NaOH in ml used for titrating the solution of the blank experiment; T is the normality of the alkali solution which was established by means of recrystallized boric acid; d is the weight of sample in g.

SUMMARY

A method has been developed for determining free boron in boron carbide and nitride; it is based on oxidation of free boron with a mixture of hydrogen peroxide and nitric acid, boron combined as nitride or boride does not react under these conditions. A titrimetric finish with alkali in the presence of invert sugar is used for determining the free boron.

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DETERMINATION OF SULFIDE, HYDROSULFIDE, AND HYDROGEN SULFIDE IN EACH OTHER'S PRESENCE IN PURE AQUEOUS SOLUTIONS

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Determination of sulfur compounds in solution is of considerable practical importance during analysis of sulfide mineral waters for the determination of the composition of sulfur dye baths and the lyes that are obtained during the sulfite method of cellulose production, in a number of industrial processes connected with the isolation of heavy metals, and also in the processes used for purifying industrial gases from hydrogen sulfide and sulfur compounds. On the other hand, the study of the numerous processes and physicochemical properties of solutions of sulfides also require reasonably reliable methods for analyzing these systems.

Methods have been published [1-17] on the determination of total sulfur belonging to sulfide, hydrosulfide, and hydrogen sulfide, both in pure solutions, and in the presence of other ions. Considerably less work has been carried out [18, 19] on the separate determination of sulfide, hydrosulfide, and free hydrogen sulfide in solution. These methods only permit the determination of sulfide and hydrosulfide in the absence of other sulfur-containing ions. Accordingly, we carried out some work on the separate determinations of sulfide, hydrosulfide, and free hydrogen sulfide.

It has been shown in a number of papers [11-14] that the use of a sulfide-silver electrode for the potentiometric titration of sulfide by silver nitrate permits a fairly accurate determination of sulfide sulfur in the presence of sulfite, sulfate, and thiosulfate ions, and also in the presence of the ions of tri- and quinquevalent arsenic compounds, since the silver sulfide that is formed during the titration has a much lower solubility product than silver arsenate and arsenite [20-27].

The method which we should like to suggest for the determination of sulfide, hydrosulfide, and hydrogen sulfide is based on the well-known potentiometric titration of the test solutions by silver nitrate using a sulfide-silver electrode, coupled with determination of the original pH of these solutions. Determination of the total sulfide in solution, and a knowledge of the pH of the solution, permits one, on the basis of simple calculations which were published in another of our papers [28], to calculate the individual contents of sulfide and hydrosulfide ions and free hydrogen sulfide in the solutions being analyzed.

It is known that precipitation of silver sulfide depends to a large extent on the pH of the medium [22, 24, 29-31]. In particular, a number of authors have pointed out [11, 14, 15] the need for making the sulfide solution alkaline when titrating with silver nitrate. However, no accurate data are available anywhere for the pH value which is necessary for obtaining reliable results.

In this connection therefore it was necessary to improve the method for determining sulfide sulfur by potentiometric titration of sodium sulfide solutions with silver nitrate solution. The results which we obtained during this work are given below.

0.05 and 0.1 M sodium sulfide solutions which were prepared from chemically pure $Na_2S \cdot 9H_2O$ were used in our experiments. The purity of the preparation was controlled iodometrically by taking aliquots of the material,

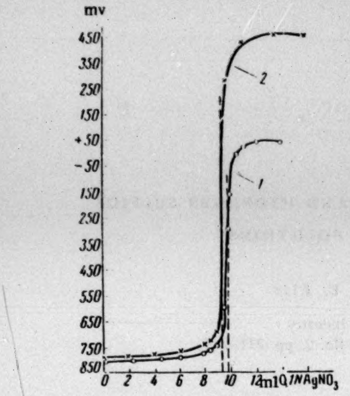

Fig. 1. Potentiometric titration curves obtained during titration of about 0.1 M Na_2S solution with $AgNO_3$ solution using a Ag/Ag_2S electrode. 1) With addition of alkali; 2) without addition of alkali.

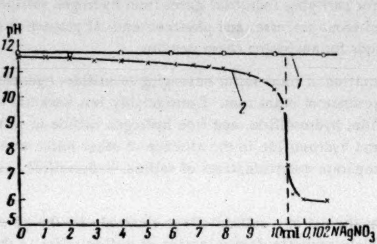

Fig. 2. Curves obtained during potentiometric titration of about 0.1 M Na_2S solution with $AgNO_3$ solution using a glass electrode. 1) With addition of alkali; 2) without addition of alkali.

and also by potentiometric titration with sulfuric acid using a glass electrode. Two sections were clearly observed on the titration curves, they correspond to the following processes:

$$S^{2-} + H^+ \rightleftarrows HS^-; \quad HS^- + H^+ \rightleftarrows H_2S.$$

The amount of sulfide determined according to the potentiometric titration curve, corresponded, within the limits of experimental error, to that determined in the same aliquot by an iodometric method, and to the results of gravimetric analysis. The concentration of the silver nitrate solutions was checked by potentiometric titration with a standard solution of sodium sulfide using a silver chloride electrode. All determinations were carried out with a Raps potentiometer, the accuracy with which the potential was measured being not less than ± 1 mv. During titration the following galvanic circuit is established:

$$\mathrm{Hg}\,|\,\mathrm{HgCl_2}\,|\,\overset{\mathrm{KCl}}{\mathrm{satd.}}\,|\text{ test solution}\,|\,\mathrm{Ag_2S}\,|\,\mathrm{Ag}$$

The sulfide-silver electrode used for titration was a platinum disc fused into a glass tube and covered with a layer of silver sulfide by treating an electrolytically deposited film of silver with sodium sulfide in solution.

Initially, a series of determinations of total sulfide was carried out in a solution of sulfide with and without addition of alkali. During the experiments the vessel containing the test solution, the buret with the titrant, and the calomel electrode were all placed in an air thermostat whose temperature was automatically controlled. The experiments were carried out at 25 ± 0.5°. In those cases where alkali was used, 10 ml of 0.1 N NaOH was added to 5 ml of the Na_2S solution.

In Fig. 1 is shown the curves obtained during potentiometric titration with and without added alkali Results of comparative determinations of the total sulfide content by an iodometric method, and by the potentiometric method, with and without addition of alkali, are also given in Table 1. It is clear from these results that the results obtained by potentiometric determination of total sulfide coincide with those obtained by the iodometric method within the limits of experimental error only in those cases where alkali is added to the test solution. When no alkali is added the titration curves are displaced towards the left. In such cases the deviation between the results of the potentiometric determinations and the iodometric determinations is 5%.

In order to elucidate the reason for this deviation, sodium sulfide was titrated using a glass electrode. The galvanic circuit was the same as before, but the sulfide-silver electrode was replaced by a glass electrode (a LP-5 potentiometer). The curves obtained in this case are shown in Fig. 2. They show that when alkali is not specially added, titration of Na_2S solution with silver nitrate is accompanied by a gradual drop in the pH of the solution. A particularly sharp pH drop is observed on approaching the equivalence point. As is evident from the titration curve, the pH of the solution being titrated drops from 11.6 to 5.9.

TABLE 1

Determination of Total Sulfide Iodometrically and by Potentiometric Titration with Addition of Sodium Hydroxide

Sodium sulfide found, mole/liter		Deviation, %
iodometrically	potentiometrically	
0,0496	0,0486	2,0
0,0496	0,0486	2,0
0,1002	0,1000	0,2
0,1002	0,0989	1,3
0,1002	0,1000	0,2
0,1002	0,1000	0,2
0,1024	0,1020	0,4
0,1024	0,1020	0,4
0,1009	0,1000	1,0
0,1009	0,1009	0,0
0,1012	0,1009	0,3
0,1012	0,1009	0,3
0,1011	0,1009	0,2
0,1011	0,1009	0,2
	Mean	0,6

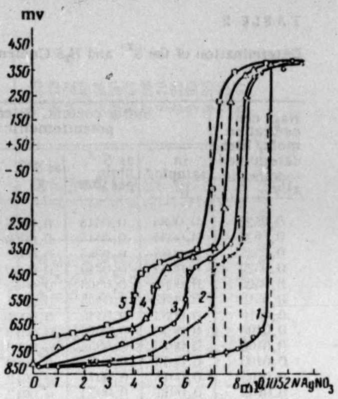

Fig. 3. Curves obtained during potentiometric titration of about 0.1 M Na_2S solution with $AgNO_3$ solution using a Ag/Ag_2S electrode. 1) Without addition of H_2SO_4; 2) 2 ml of 0.1 N H_2SO_4 added; 3) 3 ml of 0.1 N H_2SO_4 added; 4) 4 ml of 0.1 N H_2SO_4 added; 5) 5 ml of 0.1 N H_2SO_4 added.

It is known [28] that reactions of the type $S^{2-} + H^+ \rightleftharpoons HS^-$ and $HS^- + H^+ \rightarrow H_2S$ are possible. This fact gives one grounds for suggesting that under the conditions where the Na_2S solution is titrated in the absence of sodium hydroxide added specially, formation of various amounts of AgHS may occur in addition to precipitation of Ag_2S. It would be possible in this way to explain the deviation between the two methods of analysis indicated above. The following equilibria may affect the experimental results:

1. $S^{2-} + H_2O \rightleftarrows HS^- + OH^-$,
2. $HS^- + 2Ag^+ \rightleftarrows Ag_2S + H^+$,
3. $HS^- + Ag^+ \rightleftarrows AgHS$,
4. $H^+ + OH^- \rightleftarrows H_2O$,
5. $HS^- + H^+ \rightleftarrows H_2S$,
6. $Ag^+ + H_2S \rightleftarrows AgHS + H^+$

The possibility of formation of the compound AgHS as a result of reactions (3) and (6) is confirmed by direct thermodynamic calculations. According to Treadwell and Hepenstrick [22] the equilibrium constant of reaction (6) is equal to 1.76×10^9. From this it follows that the change in the isobaric potential of the system during this reaction is equal to: $\Delta Z_{(6)} = -12.6$ kcal/mole, which indicates that there is a high probability of this reaction occurring. Since the standard changes in the isobaric potential for the processes of formation of Ag^+ and H_2S are known, then the value of ΔZ^0_{AgHS} can be calculated as follows:

$$\Delta Z_{(6)} = \Delta Z^0_{AgHS} - \Delta Z^0_{Ag^+} - \Delta Z^0_{H_2S} - 12,6 = \Delta Z^0_{AgHS} + 18;4 + 6,5.$$

From which

$$\Delta Z^0_{AgHS} = -37,5 \text{ kcal/ mole}$$

$$\Delta Z^0_{(3)} = -37,5 - 3 + 18,4 = -22,1 \text{ kcal/ mole.}$$

TABLE 2

Determination of the S^{2-} and H_2S Contents by the Iodometric and Potentiometric Methods

Na_2S concentration mole/liter, determined iodometrically	Sulfur content, determined potentiometrically					Total amount of sulfur**, g	Deviations between the iodometric and potentiometric results, %
	in sample,* g	as S^{-2}, mole per liter	as S^{-2}, g	as HS^-, mole per liter	as HS^-, g		
0,0523	0,0084	0,0415	0,0066	0,0100	0,0018	0,0082	−2,3
0,0523	0,0084	0,0415	0,0066	0,0100	0,0018	0,0082	−2,3
0,0523	0,0084	0,0365	0,0058	0,0160	0,0026	0,0084	0,0
0,0523	0,0084	0,0315	0,0050	0,0220	0,0035	0,0085	+1,1
0,0523	0,0084	0,0263	0,0042	0,0255	0,0041	0,0083	−1,1
0,0510	0,0082	0,0445	0,0071	0,0070	0,0011	0,0082	0,0
0,0510	0,0082	0,0445	0,0071	0,0070	0,0011	0,0082	0,0
0,0100	0,0016	0,0073	0,0012	0,0028	0,0004	0,0016	0,0
0,0100	0,0016	0,0055	0,0009	0,0048	0,0007	0,0016	+3,0
0,0100	0,0016	0,0055	0,0009	0,0048	0,0007	0,0016	+3,0
0,0109	0,0017	0,0074	0,0012	0,0032	0,0005	0,0017	0,0
0,0109	0,0017	0,0073	0,0012	0,0038	0,0006	0,0018	+3,0
0,0109	0,0017	0,0053	0,0008	0,0054	0,0009	0,0017	+3,0
0,1015	0,0162	0,0700	0,0112	0,0300	0,0048	0,0160	−1,2
0,1009	0,0161	0,0860	0,0138	0,0160	0,0026	0,0160	+1,2
0,1015	0,0162	0,0705	0,0113	0,0280	0,0045	0,0158	−2,4
0,1015	0,0162	0,0600	0,0096	0,0430	0,0069	0,0165	+1,2
0,1015	0,0162	0,0600	0,0096	0,0429	0,0067	0,0163	+0,9
0,1015	0,0162	0,0485	0,0077	0,0550	0,0088	0,0165	+1,2
0,1015	0,0162	0,0400	0,0064	0,0600	0,0096	0,0160	−1,2
0,1000	0,0160	0,0780	0,0125	0,0240	0,0038	0,0163	+1,8
0,1000	0,0160	0,0780	0,0125	0,0240	0,0038	0,0163	+1,8
0,1000	0,0160	0,0680	0,0109	0,0340	0,0054	0,0163	+1,8
0,1000	0,0160	0,0680	0,0109	0,0340	0,0054	—	+1,8
						Mean	−0,4

*Determined iodometrically.

**Determined potentiometrically.

Accordingly, formation of AgHS at a certain hydrogen ion concentration of the test solution is fully possible thermodynamically.*

On adding alkali to the original sulfide solution, only Ag_2S is precipitated, and there is no deviation between the results of the iodometric and potentiometric methods. It follows from the series of experiments carried out that the pH of the original test solution should not be less than 13 in order to get such agreement. The difference between the solubility products of Ag_2S and Ag_2O [32] is sufficiently great ($L_{Ag_2S} = 5.5 \times 10^{-51}$, $L_{Ag_2O} = 2.0 \times 10^{-8}$), and, accordingly, addition of known amounts of alkali sufficient to keep the medium alkaline should not interfere during titration with the sulfide determination.

The method for separate determination of sulfide, hydrosulfide, and hydrogen sulfide consisted of the following. First of all the pH of the original solution was determined. A known amount of NaOH or KOH solution free from carbonate was then added to the test solution in order to establish the pH of the solution at 13. The solution was then titrated potentiometrically with the sulfide-silver electrode. From this curve total S^{2-} HS^-, and H_2S was determined (c_0). The following calculations were then carried out depending on the original pH: for pH < 9.0 (in solutions containing H_2S and HS^-)

$$c_{H_2S} = c_0 N_{H_2S} = c_0 \frac{a_{H^+} \cdot f_{a_{HS^-}}}{K_1 + a_{H^+} \cdot f_{a_{HS^-}}}, \quad c_{HS^-} = c_0 (100 - N_{H_2S}) \text{ g-ion/liter.}$$

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*Calculation shows that at pH < 9 in the solution, there are hardly any S^{2-} ions in solution, and that all the sulfide is present in the form of HS^- ions or a mixture of HS^- and H_2S.

TABLE 3

Calculation of the Solubility Product of AgHS on the Basis of the Curves Obtained during Potentiometric Titration at 25° of Na_2S Solution with Silver Nitrate using a Glass Electrode

pH	$\frac{mAg^+}{2}$	$c'_{S^{2-}}$ mole/liter	c'_{HS^-} mole/liter	c_{Na^+} mole/liter	c_{NO^-} g-ion/liter	μ	$f_{a_{HS^-}}$	$f_{a_{S^{2-}}}$	a_{HS^-}	$a_{S^{2-}}$	$a_{Ag^+}\cdot 10^{24}$	$L_{AgHS}\cdot 10^{27}$
12,16	0,0012	0,0050	0,0060	0,0246	0,0025	0,0224	0,8389	0,4952	0,0050	0,0025	1,50	7,50
12,05	0,0025	0,0038	0,0057	0,0240	0,0050	0,0218	0,8412	0,5007	0,0048	0,0019	1,70	8,16
11,90	0,0037	0,0026	0,0054	0,0234	0,0074	0,0213	0,8428	0,5044	0,0045	0,0013	2,05	9,22
11,82	0,0050	0,0018	0,0047	0,0230	0,0100	0,0211	0,8435	0,5063	0,0039	0,0009	2,47	9,63
11,70	0,0062	0,0012	0,0038	0,0224	0,0124	0,0209	0,8443	0,5082	0,0032	0,0006	3,02	9,66
11,65	0,0075	0,0007	0,0028	0,0220	0,0150	0,0208	0,8445	0,5086	0,0024	0,0003	3,96	9,50
11,52	0,0087	0,0003	0,0017	0,0214	0,0174	0,0205	0,8457	0,5114	0,0014	0,0001	6,05	8,47
12,16	0,0012	0,0051	0,0060	0,0246	0,0025	0,0224	0,8389	0,4952	0,0050	0,0025	1,50	7,50
12,05	0,0025	0,0038	0,0057	0,0240	0,0050	0,0218	0,8412	0,5007	0,0048	0,0019	1,70	8,16
11,90	0,0037	0,0026	0,0054	0,0234	0,0074	0,0213	0,8428	0,5044	0,0045	0,0013	2,05	9,22
11,82	0,0050	0,0018	0,0047	0,0230	0,0100	0,0211	0,8435	0,5063	0,0039	0,0009	2,47	9,63
11,70	0,0062	0,0012	0,0038	0,0224	0,0124	0,0209	0,8443	0,5082	0,0032	0,0006	3,02	9,66
11,65	0,0075	0,0007	0,0028	0,0220	0,0150	0,0208	0,8445	0,5086	0,0024	0,0003	3,96	9,50
11,52	0,0087	0,0003	0,0017	0,0214	0,0174	0,0205	0,8457	0,5114	0,0014	0,0001	6,05	8,47
									Mean		$(8,87\pm 0,21)\cdot 10^{-27}$	

For pH > 9.0 (in the presence of HS^- and S^{2-} in solution)

$$c_{HS^-} = c_0 N_{HS^-} = c_0 \frac{a_{H^+} \cdot f_{a_{HS^-}}}{K_2 f_{a_{HS^-}} + a_{H^+} f_{a_{S^{2-}}}}\ ;\ c_{S^{2-}} = c_0 (100 - N_{HS^-}).$$

where c_{HS^-}, c_{H_2S}, and $c_{S^{2-}}$ are the concentrations of the corresponding ions and free hydrogen sulfide in mole/liter or g.ion/liter; N_{HS^-}, N_{H_2S} are the molal ratios as % of HS^- ions and hydrogen sulfide; K_1, K_2 are the constants of the first and second stages of dissociation of H_2S; α_{H^+} is the hydrogen ion activity; $f\ \alpha_{HS^-}$, $f\ \alpha_{S^{2-}}$ are the activity coefficients of the corresponding ions.

In order to study the behavior of sulfide solutions at pH < 12 we carried out a series of titrations of about 0.1, 0.05, and 0.01 M Na_2S solutions with silver nitrate, various amounts of alkali being added. 5 ml or 10 ml of solution was taken for titration and various amounts of 0.1, 0.05, and 0.01 N H_2SO_4 added, the amount of the latter added being dependent on the sodium sulfide concentration.

As is evident from Fig. 3, two breaks appear on the titration curve on addition of acid. As the amount of acid added is increased, the first break appears on addition of smaller amounts of $AgNO_3$.

On the basis of these results we assumed that the first sloping part on the curves corresponds to deposition of Ag_2S from solution, while the second corresponds to deposition of AgHS. In order to confirm this we calculated the equivalents of S^{2-} and HS^- corresponding to each of the breaks, and then compared the sum of these values with the total original content of sulfide in the same solution as determined iodometrically. If our assumptions were correct, then the sums of the equivalents should coincide.

From Table 2 it is clear that the total S^{2-} and HS^- content as determined potentiometrically, actually corresponds, within the limits of possible experimental error, to the sulfide sulfur content determined iodometrically. Consequently, both the thermodynamic calculations and experimental data confirm the assumption of the formation of silver hydrosulfide under the experimental conditions used. Results obtained during potentiometric titration of sulfide with silver nitrate using a glass electrode were used for calculating the solubility products.

Each point on the curve corresponds to the equilibrium $S^{2-} + H^+ \rightleftharpoons HS^-$. Accordingly $\alpha_{S^{2-}}/\alpha_{HS^-} = K_2/\alpha_{H^+}$ or $f_{\alpha_{S^{2-}}} c'_{S^{2-}} / f_{\alpha_{HS^-}} c^1_{HS^-} = K_2/c_{H^+}$; where K_2 is the second dissociation constant of H_2S; $c^1_{S^{2-}}$ and $c^1_{HS^-}$ the concentrations of the S^{2-} and HS^- ions in g. ion/mole which are different for each point on the curve; $\alpha_{S^{2-}}$ and α_{HS^-} are the activities of these ions; and $f_{\alpha_{S^{2-}}}$ and $f_{\alpha_{HS^-}}$ are the activity coefficients of the corresponding ions.

Formation of a precipitate during titration is determined by the following equilibria:

$$S^{2-} + 2Ag^+ \rightleftharpoons Ag_2S$$
$$HS^- + Ag^+ \rightleftharpoons AgHS.$$
$$AgHS + Ag^+ \rightleftharpoons Ag_2S + H^+$$

If the sulfide concentration of the original solution is designated by x, then, on addition of m moles of $AgNO_3$, total $c'_{S^{2-}} + c'_{HS^-} = x - m_{Ag^+}/2$. The solubility product of AgHS is given by $L_{AgHS} = \alpha_{Ag^+}\ \alpha_{HS^-}$. The activity of the ions α_{Ag^+} is determined from the solubility product of Ag_2S. Since $x = c'_{S^{2-}} + c'_{HS^-}$ and α_{H^+} are known, it is not difficult to calculate $\alpha_{S^{2-}}$ and from this $\alpha_{Ag^+} = \sqrt{L_{Ag_2S}/\alpha_{S^{2-}}}$. During calculation of α_{H^+} on the basis of the results obtained during potentiometric titration with a glass electrode in the alkaline region, a correction was applied for the deviation of the readings of the glass electrode from the normal hydrogen function [28]. The activity coefficients were calculated from the Debye-Huckel equation for dilute solutions [33,34]. Table 3 contains the results obtained for the solubility product of AgHS calculated in this way. The mean value L_{AgHS} at 25° was found to be $(8.87 \pm 0.21) \times 10^{-27}$.

SUMMARY

A method is suggested for the determination of sulfide, hydrosulfide, and hydrogen sulfide in pure solutions; it is based on the potentiometric measurement of the pH of these solutions, with subsequent addition of known amounts of pure alkali to establish a pH of 13, and titration of these alkaline solutions with silver nitrate. By means of the appropriate thermodynamic equations the concentrations of S^{2-}, HS^-, and H_2S are then calculated from the results obtained.

It has been established that silver hydrosulfide is formed as well as silver sulfide during titration of sulfide solutions. The solubility product of silver hydrosulfide at 25° has been calculated. It was found to be equal to $(8.87 \pm 0.21) \times 10^{-27}$.

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IDENTIFICATION OF DITHIZONE AND ITS ORTHO- AND PARA-METHYL DERIVATIVES

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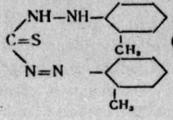
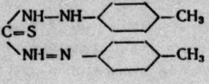
There are no satisfactory methods for identifying diphenylthiocarbazone (dithizone), o-ditolylthiocarbazone• (I) and p-ditolylthiocarbazone• (II).


(I)


(II)

The melting points of these materials are close and depend on their purity. The insignificant difference in the colors of their inner-complex salts can also lead to mistaken conclusions unless the operator is experienced.

For identification of the compounds listed, use can be made of differences in their solubilities in aqueous alkali solutions, and of the difference in the stability of the bonds formed between metals and the acid residues in the inner-complex salts formed by these compounds [1, 2]. Dithizone dissolves in aqueous alkaline solutions at lower pH values than does its methyl derivatives. Thus, on shaking the green solution of dithizone in carbon tetrachloride with an equal volume of an aqueous solution with a pH of 9-9.5, the greater part of the dithizone is extracted into the aqueous phase, coloring it an orange-yellow color, while the carbon tetrachloride phase becomes almost completely colorless [3]. Under these conditions, the methyl derivatives are extracted to such a small extent from the carbon tetrachloride that the aqueous layer does not acquire an appreciable color, or acquires only a weakly yellowish color on prolonged shaking.

In order to establish more clearly the differences in the stability of the bonds of zinc with the acid residues in the inner-complex salts of dithizone and its methyl derivatives, the following exchange reactions were studied: a) the exchange reactions of the zinc inner-complex salts of all three compounds with hydrogen sulfide and solutions of sodium and ammonium sulfides, and b) of dithizone and its methyl derivatives with zinc sulfide.

For these experiments 10^{-4} M solutions of dithizone and its analogs, 5×10^{-5} M solutions of the zinc complexes of these compounds in carbon tetrachloride, and 0.1 M solutions of hydrogen sulfide and ammonium and sodium sulfide were used.

•The ortho- and para-ditolylthiocarbazones are henceforth called o- and p-ditolyzones and are arbitrarily designated: o-HDtz and p-HDtz as monobasic acids.

a) Behavior Toward Hydrogen Sulfide Water. On shaking solutions of the dithizonate, and o- and p-ditolyzonates of zinc with an equal volume of hydrogen sulfide water, rapid breakdown of zinc o-ditolyzonate alone occurs.

The red color of the carbon tetrachloride layer containing zinc o-ditolyzonate in solution changes to green, which is characteristic for a solution of the free o-ditolyzone in organic solvents:

$$\underset{\text{in } CCl_4}{Zn(o\text{-}Dtz)_2} + \underset{\text{in } H_2O}{H_2S} \rightleftarrows \underset{\text{in } CCl_4}{2o\text{-}HDtz} + \underset{\text{in } H_2O}{ZnS}.$$

Zinc dithizonate and p-ditolyzonate are not broken down by hydrogen sulfide water and the color of the carbon tetrachloride layer does not change.

b) Behavior Toward Sodium and Ammonium Sulfides. Zinc o-ditolyzonate is destroyed immediately by sodium sulfide with decolorization of the carbon tetrachloride layer and coloring of the aqueous layer a yellow-orange color. Zinc dithizonate is destroyed slowly on prolonged shaking (several minutes) or on standing for several hours, the same color changes occuring in the two phases.

$$\underset{\text{in } CCl_4}{Zn(o\text{-}Dtz)_2} + \underset{\text{in } H_2O}{Na_2S} \rightleftarrows ZnS + \underset{\text{in } H_2O}{2Na(o\text{-}Dtz)}$$

Zinc p-ditolyzonate is destroyed even more slowly and incompletely. Only partial breakdown occurs on standing for several weeks. The aqueous layer acquires a weak-yellow color, while the color of the carbon tetrachloride becomes somewhat lighter.

On treating solutions of the zinc complexes of these compounds in carbon tetrachloride with 0.1 M ammonium sulfide, zinc o-ditolyzonate and dithizonate are destroyed immediately. Under these conditions, in the first case the carbon tetrachloride layer becomes light yellow in color, or does not change. In the second case, the carbon tetrachloride layer is decolorized, while the aqueous layer acquires an orange-yellow color as a result of the transfer of the dithizone from the organic solvent layer into the aqueous alkaline solution in the form of its ammonium salt.

Zinc p-ditolyzonate is not destroyed even on very prolonged contact with the ammonium sulfide solution.

The properties of the zinc complexes are compared in the table.

On shaking green solutions of all three compounds in carbon tetrachloride with an aqueous suspension of zinc sulfide (freshly precipitated and aged forms) only p-ditolyzone reacted with both forms, while dithizone reacted with the freshly precipitated form of the sulfide.* In this case the green color of the CCl_4 layer changed to red:

$$\underset{\text{in } CCl_4}{2n\text{-}HDtz} + \underset{\text{in } H_2O}{ZnS} \rightleftarrows \underset{\text{in } CCl_4}{Zn(n\text{-}Dtz)_2} + \underset{\text{in } H_2O}{H_2S}$$

Dithizone did not react with the aged form of ZnS. o-Ditolyzone did not react with either of the two forms of zinc sulfide.

The fact that zinc p-ditolyzonate is not broken down by hydrogen sulfide, and the sulfides of sodium and ammonium indicates that the stability of the bond between zinc and the acid residue in zinc p-ditolyzonate is greater than the stability of the bonds between zinc and the acid residues in zinc dithizonate and o-ditolyzonate. The fact that zinc o-ditolyzonate is broken down by all the reagents indicated shows that the bond is least stable in the ortho isomer

The stability of zinc dithizonate towards hydrogen sulfide indicates the higher stability of the bond of zinc with the dithizonate ion as compared with the zinc bond in the o-ditolyzonate which is destroyed under these conditions.

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*The interaction of zinc sulfide with dithizone and of zinc dithizonate with hydrogen sulfide has been studied by A. K. Babko and A. T. Pilipenko [4].

Layer	Color of the solutions		
	$Zn(p\text{-}Dtz)_2$	$ZnDz_2$	$Zn(o\text{-}Dtz)_2$
	After treatment with hydrogen sulfide		
Aqueous	Colorless	Colorless	Colorless
CCl_4	Red-violet	Red	Green
	After treatment with sodium sulfide		
Aqueous	Colorless *	Colorless *	Yellow-orange
CCl_4	Red-violet	Red	Colorless
	After treatment with ammonium sulfide		
Aqueous	Colorless	Orange-yellow	Weak-yellow or colorless
CCl_4	Red-violet	Colorless	Green

*After a short shaking period (~ 10 sec).

The intermediate position of zinc dithizonate with respect to the stability of the zinc bonds with the acid residue as compared with its o- and p-methyl derivatives is confirmed by the fact that dithizone only reacts with freshly precipitated zinc sulfide, while p-ditolyzone reacts with its aged form as well, and o-ditolyzone does not react with either of the ZnS forms. A confirmation of the intermediate position of zinc dithizonate in this series is also found in the differences in the reactions of the zinc compounds of dithizone and its methyl derivatives with sodium sulfide.

Thus, the zinc inner-complex salts of p-ditolyzone, dithizone, and o-ditolyzone can be arranged in the following series with respect to decreasing stability of the bond between zinc and the acid residues in these compounds:

$$Zn\,(n\text{-}Dtz)_2 > ZnDz_2 > Zn\,(o\text{-}Dtz)_2.$$

All these reactions could be used for identification of dithizone, and o- and p-ditolyzone. However, the most suitable reaction for this purpose would appear to be the sharp difference in behavior of the zinc inner-complex salts of these compounds toward an ammonium sulfide solution.

For this purpose 10^{-4} M solutions of dithizone, and o- and p-ditolyzone in carbon tetrachloride are first shaken in a separating funnel with an aqueous solution of zinc acetate in order to obtain the zinc complex compounds. After removal of the aqueous layer, an equal volume of 0.1 M ammonium sulfide is added to the carbon tetrachloride layer contained in a test tube.

A change in the red color of the carbon tetrachloride to green indicates the presence of o-ditolyzone, while decolorization of the organic layer with simultaneous orange-red coloration of the aqueous layer indicates the presence of dithizone, and the absence of any effect indicates the presence of p-ditolyzone.

SUMMARY

The zinc inner-complex salts of dithizone, o-and p- ditolyldithiocarbazone can be arranged in the following series in order of the stability of the bond between zinc and the acid-residues in these complexes:

$$Zn(n\text{-}Dtz)_2 > ZnDz_2 > Zn\,(o\text{-}Dtz)_2.$$

A method is suggested for identifying dithizone and o- and p-ditolyldithiocarbazone which is based on differences in the behavior of their zinc complexes toward ammonium sulfide.

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ANALYSIS OF FLUOROORGANIC COMPOUNDS

THE USE OF PYROHYDROLYSIS FOR THE SIMULTANEOUS MICRODETERMINATION OF FLUORINE, CARBON, AND HYDROGEN

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The essence of the method which we should like to suggest, and which was developed on the basis of work published by us earlier on the analysis of fluoroorganic compounds [1-3], consists in determining carbon and hydrogen by pyrolytic combustion of an aliquot in a layer of magnesium oxide, absorption of fluorine at the moment of decomposition in the form of magnesium fluoride, hydrolytic decomposition of the latter by superheated steam at a high temperature, and titration of the fluoride ion obtained.

The capacity of halides to hydrolyze has been used several times in inorganic chemistry, for technological purposes [4-8], and thermodynamic studies [9-16]. The effect of steam at high temperature in an oxidation atmosphere is also regarded as a most efficient method for the quantitative decomposition of thermostable fluorides in the elemental analysis of fluoroorganic compounds, and has found wide application [17-21] It should be pointed out, however, that the introduction of water into the combustion sphere of the material restricts the analyst to the determination of carbon alone, and special methods are necessary to establish the amount of hydrogen [22-25]. Attempts have been made in organic analysis to determine fluorine directly by decomposition of the organic fluorides in a stream of superheated steam and to liberate fluorine as HF [26]. Such a technique has, however, been found to be applicable only to solid, nonvolatile fluorides, and, in view of numerous limitations and low accuracy [27], has not been developed further. Recently, high temperature hydrolysis or so-called "pyrohydrolysis" has been used in inorganic analysis for the determination of fluorine in heavy metals and their fluorides [28-33].

There are no clear indications in the literature as to the possibility of quantitative pyrohydrolysis of magnesium fluoride, which in its properties occupies an intermediate position between the heavy metal fluorides, which are readily broken down by steam, and the fluorides of the alkali and alkaline earth metals, which are difficult to hydrolyze and which demand the use of special catalysts to make the process quantitative. Domange [11] did not get reproducible results during the pyrohydrolysis of MgF_2, and was of the opinion that the reason for this is the sintering of MgO particles and the difficult accessibility of the material to the steam. Warf [28] on the basis of single experiments, classes magnesium fluoride as a readily hydrolyzable material, although his results clearly show that pyrohydrolysis of MgF_2 was incomplete, since the fluorine deficit corresponds to an enhanced magnesium content, as determined by Warf on the basis of the MgO residue. The fact that pyrohydrolysis of MgF_2 is incomplete was confirmed by experiments which we carried out under conditions differing from those described by both Domange and Warf. We subjected to pyrohydrolysis in a platinum tube, magnesium fluoride distributed in granules of magnesium oxide, in a layer of which combustion of a fluoroorganic compound had been carried out beforehand. During these experiments the same portion of magnesium oxide was used several times, and was placed in turn during the analysis in the combustion tube where the fluorine was absorbed, and in

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*Deceased.

TABLE 1

Preparation	No. of combus-tions	F found, %	Loss of F	
			%	mg
Magnesium oxide, analytical grade	1—3	37,09*	4,95	0,283
	4	41,83	0,21	0,012
GOST 4526-48 Kal'baum	1—4	40,68*	1,36	0,094
	5	41,86	0,18	0,013

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*Mean value.

TABLE 2

Test material*	Halogen	Halogen (Cl, Br, and I), %			Length of the MgO layer, cm
		calc.	found on the silver after combustion, MgO layer	adsorbed by the magnesium oxide**	
Hexachloroethane C_2Cl_6	Cl	89,86	3,13	86,73	8
			3,79	86,07	8
			—	89,86	14
Bromobenzoic acid $C_7H_5BrO_2$	Br	39,75	22,07	17,68	8
			17,54	22,21	8
			2,64	37,11	14
			5,53	34,22	14
Bis-iodomethyltetramethyl disiloxane $C_6H_{16}I_2Si_2O$	I	61,29	55,48	5,81	8
			57,79	3,50	8

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*All the experiments were carried out on aliquots of 4-8.5 mg.

**Calculated by difference.

the tube used for pyrohydrolysis where it was liberated as HF. The fluorine content was about 0.25% of the weight of magnesium oxide taken. The first experiments with a new (free from fluorine) magnesium oxide preparation always gave low results for fluorine in the condensate after pyrohydrolysis, but, after four to five cycles of combustion and pyrohydrolytic treatment, carried out with the same preparation of MgO, we started to get correct results for fluorine (Table 1), and subsequently, the preparation could be used with good results for an indefinitely long time. Thus, it was established that it should be possible to pyrohydrolyze magnesium fluoride quantitatively in a layer of magnesium oxide layer after appropriate treatment of the latter. In order to establish the correctness of Domange's suggestion, we carried out a combustion of a fluoroorganic compound with a new portion of magnesium oxide, pyrohydrolyzed the MgO granules after using it once, and then ground it up in an agate mortar and treated it repeatedly with steam under the same conditions. The amount of fluorine which was additionally liberated from the ground magnesium oxide amounted to about 0.5% of the fluorine, i.e., approximately one tenth of the total loss of fluorine. On pyrohydrolyzing ground-up preparations which had been used earlier in granular form, negligible amounts of fluorine were again liberated. Obviously the sintering of MgO particles on the surface of the granules bears only an insignificant share of the blame for the incomplete pyrohydrolysis of magnesium fluoride when new portions of magnesium oxide are used.

During the analysis of organic compounds containing several elements, magnesium oxide, in addition to absorbing fluorine, also absorbs other elements whose behavior during pyrohydrolysis differs. Phosphorus, silicon, and boron do not give volatile hydrolysis products. Sulfur, which is quantitatively absorbed by magnesium oxide, only partially passes into the condensate as sulfate and does not interfere with fluorine determination. Thus, during the analysis of β,β'-difluorodiethylmethylthionphosphinate, of the 1.8 mg of sulfur present in the aliquot

TABLE 3

Test material	C, %		H, %		F, %	
	found	difference	found	difference	found	difference
β,β'-Difluorodiethylmethylthionphosphinate $C_5H_{11}F_2O_2PS$	29,43	+0,01	5,41	−0,02	18,52	−0,10
Calculated C 29,42%; H 5,43%; F 18,62%	29,35	−0,07	5,41	−0,02	18,45	−0,17
Tri-(meta-nitrophenyl)oxonium borofluoride $C_{18}H_{12}BF_2N_3O_7$	46,06	−0,02	2,56	−0,02	15,74	−0,46
	46,19	+0,11	2,66	+0.08	15.74	−0,46
Calculated C 46,08%; H 2,58%; F 16,20%						
Anilide of α-hydroperfluoroisobutyric acid + diethylsilanediol	41,92	+0,07	6,72	−0,08	18,32	+0,16
$C_{10}H_7F_6NO + C_4H_{12}SiO_2$	42,19	+0,07	6,35	+0,03	21,26	+0,22
1) C 41,85%; H 6,80%; F18,48% 2) C 42,12%; H 6,32%; F21,04%						
1,1-Dibromo-2,3,3-trifluorochloro-3-bromopropane	9,65	−0,18	0,25	−0,02	15,42	−0,02
$C_3HBr_3ClF_3$	9,75	−0,01	0,34	+0,07	15,22	−0,22
Calculated C 9,76%; H 0,27%; F 15,44%						
The hydrate of the ethylamide of α,γ,γ-trifluoro-γ-chloroacetoacetic acid	30,59	—	3,80	−0,05	23,97	−0,22
$C_6H_9ClF_3NO_3$	30,46	−0,13	3.73	−0.12	24,11	−0.08
Calculated C 30,59%; H 3,85%; F 24,19%						

Note: All the analyses were carried out with aliquots of 4-9 mg; the length of the magnesium oxide layer was 8 cm.

only 0.658 mg was found in the hydrolyzate (by difference between the results of acidimetric and thorimetric [34] titration). The extent to which chlorine, bromine, and iodine are absorbed by magnesium oxide decreases with increasing atomic weight of the halogen. We used the method of determining halogen in a case [35], in order to establish what are the amounts of the various halogens that pass into the silver after combustion of several materials in a magnesium oxide layer (Table 2). In view of the manifest absorption of appreciable amounts of chlorine and bromine by magnesium oxide, we checked on the possibility of determining carbon and hydrogen in halogen derivatives without using a platinum catalyst, and obtained satisfactory results (Table 3). Obviously, the presence of small amounts of halogen in the gaseous products of pyrolytic combustion issuing from the tube containing MgO does not exhibit an inhibiting action on the oxidation of CO to CO_2 [36] in the oxidizing zone of the combustion tube.

At the same time it was shown that magnesium chloride can be quantitatively pyrohydrolyzed, and determined together with fluoride by titrating an aliquot of the hydrolyzate (Table 4).

Examples of simultaneous determination of F, C, and H in various fluoroorganic compounds are given in Table 3.

In the method suggested it was found expedient to combine the usual methods of elemental analysis, i.e., combustion in a quartz tube, with the possibility of a further quantitative liberation of fluorine. For this purpose it was important to make a correct evaluation of the loss of fluorine arising from its interaction with quartz at a high temperature. This interaction has not been examined under the conditions used for elemental analysis of fluorides, and there is no unanimous opinion on this question. While one analyst thinks that heating a fluoride in a quartz tube forms not only hydrogen fluoride and silicon tetrafluoride, but entrains a certain amount of

TABLE 4

Test material	C, %		H, %		Cl, %		F, %	
	found	difference	found	difference	found	difference	found	difference
Monohydromonochloroperfluoroethylene	20,33	+0,02	0,29	—0,14	14,94	—0,05	64,12	—0,13
C_4HClF_8 Calc. C 20,31%; H 0,43%; Cl 14,99%; F 64,27%	20,51	+0,20	0,46	+0,03	15,26	+0,27	63,94	—0,33
α-Difluorochloro-β-dichlorofluoroethylene	12,94	+0,12	0,04	+0,04	56,78	+0,03	30,35	—0,07
$C_2Cl_3F_3$ Calc. C 12,82%; Cl 56,75%; F 30,42%	12,73	—0,09	0,05	+0,05	56,50	—0,25	30,30	—0,12

Note: All the analyses were carried out with aliquots of 5–7 mg; the length of the magnesium oxide layer was 8 cm.

TABLE 5

Fluorine found by pyrohydrolytic treatment, %					Total, %	Calc. %	Difference, %
quartz tube fragment	broken lumps of quartz	broken quartz etched with alkali	magnesium oxide from the case	magnesium oxide from test tube			
0,65*	—	—	51,67	—	52,32	52,39	—0,07
0,41**	—	—	41,40	—	41,81	42,04	—0,23
2,16**	3,50	—	36,15	—	41,81	42,04	—0,23
2,00**	5,60	—	34,14	—	41,74	42,04	—0,30
1,89*	—	11,39	38,72	—	52,40	52,39	+0,01
0,59*	—	18,46	23,40	—	42,45	42,04	+0,41
—	—	—	—	52,63	52,63	52,39	+0,24
—	—	—	—	52,51	52,51	52,39	+0,12

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*Combustion of the amide of α-hydroperfluoropropionic acid.

**Combustion of the anilide of α-hydroperfluoroisobutyric acid.

the fluorine by quartz in the form of nonvolatile compounds [37-39], others have not observed this phenomenon [26, 40]. Our earlier attempts at determining C, H, and F, by absorbing the latter inside the combustion tube, led us to the conclusion that it is impossible to liberate the fluorine completely from the quartz combustion apparatus in a stream of oxygen. We demonstrated the presence of fluorine in the apparatus by means of the following experiments. In an empty combustion tube was placed a quartz case filled in its narrow part with magnesium oxide granules, a test tube 9 cm long containing an aliquot of fluoride was then fitted into the case, so that the edge of the test tube touched the MgO in the case. When combustion was complete the test tube was broken up and the lumps of quartz subjected to pyrohydrolysis. The magnesium oxide was pyrohydrolyzed separately. 2) The experiment was repeated with a layer 8 cm long of broken quartz 1-2 mm in size in the test tube. The broken bits of the test tube, the quartz lumps, and the MgO from the case were pyrohydrolyzed separately. 3) The same experiments were repeated using broken quartz etched beforehand with alkali and then washed with acid and water. 4) The test material was ignited in a tube filled with magnesium oxide; after combustion the MgO was strewn into the tube used for pyrohydrolysis, while the test tube was broken up and the fragments pyrohydrolyzed separately. As is evident from the results given in Table 5, it was established experimentally in the course of these experiments that fluorine is absorbed by quartz during pyrolytic combustion of fluoroorganic compounds, and that there exists a relation between the amount of fluorine absorbed and the magnitude of the quartz surface. It was established at the same time that during combustion of a fluoride in a test tube filled with magnesium oxide, that fluorine is not absorbed on the quartz walls of the test tube, and that the traces of magnesium oxide remaining on the test tube walls after strewing the MgO do not contain appreciable amounts of fluorine; consequently, strewing the MgO granules, after combustion of the fluoroorganic compound, from the test tube into the tube used for pyrohydrolysis, cannot be a source of error during fluorine determination.

The observations described above have been used for developing a method for the simultaneous determination of fluorine, carbon, and hydrogen.

SUMMARY

It has been established that fluorine absorbed by magnesium oxide during combustion of fluoroorganic compounds can be quantitatively liberated by pyrohydrolysis, and can be determined by titration.

It has been established that during combustion of fluoroorganic compounds in the absence of magnesium oxide, the fluorine is absorbed by quartz in amounts which are proportional to the surface area of the quartz, and can be liberated by pyrohydrolysis.

It has been shown that it is possible to carry out a simultaneous microdetermination of carbon, hydrogen, and fluorine in various heteroorganic compounds; nitrogen, phosphorus, silicon, boron, sulfur, chlorine, and bromine do not interfere with fluorine determination.

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REFRACTOMETRIC DETERMINATION OF TERTIARY BUTANOL IN COMPLEX MIXTURES WITH WATER AND THE SECONDARY AND PRIMARY ALCOHOLS

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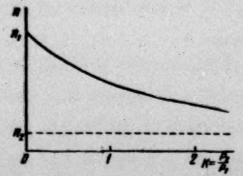
The few methods used for the selective determination of tertiary alcohols in mixtures with secondary and primary alcohols are based on the considerably easier dehydration of the tertiary alcohols in the presence of catalysts (zinc chloride, iodine, p-toluene sulfonic acid, ascanite, etc). These methods have been developed in the main for tertiary terpene alcohols used in the perfumery industry (linalool, terpineol). The amount of water liberated during dehydration is determined either by measuring its volume after distillation with aromatic hydrocarbons in a standard Dean and Stark apparatus [1, 2], or by titrating with Fischer reagent [3]. Methods based on dehydration take a considerable time, are unsuitable for the analysis of mixtures with appreciable water contents, and are not accurate enough. The Denige reaction has been recommended for the determination of tertiary butanol [4, 5].

We should like to suggest for the selective determination of tertiary butanol its conversion into tertiary butyl chloride by the action of hydrochloric acid. It is known that the rate of interaction of tertiary alcohols with the hydrogen halides $ROH + HX = RX + H_2O$ is some orders higher than the reaction rate of the secondary and primary alcohols with them.

Tertiary alcohols react so rapidly with concentrated hydrochloric acid, that at room temperature a layer of the tertiary alkyl chloride separates out as a layer from the hydrochloric acid solution in a matter of minutes. Under the same conditions primary and secondary alcohols do not react appreciably, and prolonged heating is necessary to convert them into the chlorides. This reaction is used for detecting tertiary alcohols [6, 7], but the possibility of using it for quantitative analysis has not been studied at all. The main difficulty in this connection is the determination of small amounts of liquid tertiary chlorides in heterogeneous mixtures with excess hydrochloric acid. However, the problem of determining the components of liquid heterogeneous systems can be successfully solved in many instances by the unique technique of refractometric analysis,which has hardly been used hitherto. Essentially the method reduces to the fact that for the determination of the amount of one of the coexisting liquid phases in a heterogeneous system, it is sufficient to add an exact amount of a liquid which is miscible with the phase to be determined and is completely insoluble in the other phase, and then measure the refractive index of the mixture formed. The amount of one of the components of the binary mixture obtained can be determined by means of a curve relating the refractive index of the mixture to the ratio of the amounts (concentrations) of the components $K = P_2/P_1$. In these coordinates the curve approximates very closely to a hyperbola starting at the ordinate axis at a point corresponding to the refractive index of the liquid added n_1, and then approaches the refractive index of the phase to be determined n_2 (see diagram).

In order to ensure a sufficiently high accuracy, the liquid to be added must be chosen with care, it should differ strongly in its refractive index from the test liquid and be similar to it in volatility, since no change in



The relation between the refractive index of binary mixtures and the ratio of the amounts of the components (P_1 and P_2 are the amounts of the components, n_1 and n_2 are the refractive indices).

composition should occur during transference of a sample to the refractometer. For the determination of tertiary butyl chloride (b.p. 51°, n^{20}_D 1.3852), benzene satisfies these conditions most closely (b.p. 80°, n^{20}_D 1.5012).

Thus, in order to determine the amount of the tertiary chloride P_x which separates out as a layer from the hydrochloric acid solution of the alcohols, it is sufficient to add an aliquot of benzene P to the heterogeneous mixture of the chloride and the hydrochloric acid solution, mix (shake) the whole and then measure the refractive index of the upper (chloride-benzene) layer. In order to simplify calculation it is best to plot on the working curve, not the ratio P_x/P, but the direct ratios of the amounts of the tertiary alcohol being determined and the benzene added $K = P_{\text{tert. alcohol}}/P$. Then, having read off the value K corresponding to the measured refractive index of the benzene layer when an aliquot P of benzene had been added and an aliquot A of the test material had been taken, the content of the tertiary alcohol in percent C can be found by means of the formula $C = 100\,K\,P/A$.

In order to completely exclude possible errors which may arise because of incomplete conversion of the tertiary alcohol into the chloride under the experimental conditions used, it is better to use the curve obtained in experiments with the pure tertiary alcohol or solutions of it of known concentration, rather than the refractive index curve obtained with mixtures of the tertiary chloride and benzene.

An experimental check completely confirmed the applicability of the principle of refractometric analysis set forth above to the selective determination of tertiary butanol. The technique described in the experimental part was checked on mixtures containing from 5 to 80% of tertiary butanol in the presence of appreciable amounts of other alcohols and water. As is evident from the results given in Table 1, the experimental accuracy of the determination of tertiary butanol by the method suggested amounts to 0.2-0.4% on an average, even in the presence of 16 times its amount of primary and secondary alcohols. Using this technique only a few decigrams of a mixture is necessary and a determination takes about 20 minutes.

TABLE 1

Determination of Tertiary Butanol in the Presence of Primary and Secondary Butanol

Components of the mixture (apart from tertiary butanol) and the ratio of their concentrations	Tertiary butanol %, wt.		Absolute exptl. error, %
	taken	found	
Secondary butanol, n-butanol (1 : 3)	25,2	25,2	0,0
Secondary butanol, water (1 : 2)	18,5	18,4	−0,1
Secondary butanol, isobutanol (1 : 1)	58,7	58,7	0,0
Isobutanol, methanol (2 : 3)	35,7	35,3	−0,4
Secondary butanol, propanol (1 : 1)	41,2	41,4	+0.2
Secondary butanol, isobutanol, n-butanol (5 : 4 : 5)	33,3	32,7	−0,6
Secondary butanol	58,5	57,8	−0,7
Isobutanol	58,8	59,7	+0,9
Secondary butanol, methanol (2 : 5)	48,4	28,5	+0,1
Secondary butanol, isobutanol, n-butanol (2 : 1 : 1)	18,8	19,1	+0,3
Secondary butanol, isobutanol, n-butanol, water (8 : 4 : 4 : 3)	5,0	5,3	+0,3
Secondary butanol, isobutanol, n-butanol (2 : 1 : 1)	79,5	78,6	−0,9
Secondary butanol	77,6	78,0	+0,4

TABLE 2

Results used for Constructing the Curve Relating the Calculating Coefficient K to the Refractive Index of the Benzene Layer

Ratio of the aliquot of tertiary butanol to benzene, K	Refractive index of the benzene layer, n_D^{20}	Ratio of the aliquot of tertiary butanol to benzene, K	Refractive index of the benzene layer, n_D^{20}
0	1,5012	0,604	1,4522
0,0735	1,4911	0,640	1,4500
0,1385	1,4840	0,762	1,4452
0,228	1,4750	0,836	1,4420
0,287	1,4713	1,036	1,4360
0,440	1,4606	1,223	1,4324

EXPERIMENTAL

Development of an experimental technique reduced to establishing the conditions which will ensure quantitative conversion of tertiary butanol into the chloride, and under which the isomers do not react with hydrochloric acid, and are not extracted by benzene from the aqueous layer.

Preliminary experiments were carried out with 50% solutions of pure preparations of all four isomeric butanols in cryoscopic benzene. 0.5-1 ml samples were measured out with a micropipet into test tubes with ground-glass stoppers, the samples were then mixed with concentrated hydrochloric acid and vigorously shaken; the refractive index of the benzene layer was then determined. The volume of hydrochloric acid was varied from 3 to 10 ml, while the time for which the shaking was carried out was varied from 3 to 12 minutes. The refractive index of the benzene layer served as a criterion that the formation of the chlorides had gone to completion, and that the extraction of the alcohols was complete; under the optimum conditions, the refractive index of the benzene layer in experiments with tertiary butanol should be a minimum, while in experiments with its isomers, on the other hand, it should be a maximum and should be as close as possible to the refractive index of pure benzene.

These preliminary experiments showed that concentrated hydrochloric acid, although it does not react with the secondary and primary alcohols under the conditions indicated, does not extract them completely from the benzene layer (n_D^{20} of the upper layer was $10\text{-}15 \times 10^{-4}$ less than for pure benzene, and only on repeated treatment with the acid did the refractive index agree with that of benzene). Since it had been established previously that under analogous conditions the alcohols are quantitatively extracted from a benzene solution by 80% sulfuric acid [8], mixtures of hydrochloric acid containing varying amounts of concentrated sulfuric acid were tested to get complete extraction of the unreacted primary and secondary alcohols. Optimum results were given when a mixture of two volumes of concentrated hydrochloric acid and one volume of 80% H_2SO_4 was used, and the time for which the shaking was carried out was 5 minutes. Under these conditions almost complete conversion of tertiary butanol to the chloride was achieved, with negligible conversion of the primary and secondary alcohols, and complete extraction of the latter from the benzene layer.

Treatment of 50% benzene solutions of a number of simple organic oxygen-containing compounds with the acid mixture indicated showed that methanol, ethanol, and propanol, and also acetic acid, do not interfere with the determination of tertiary butanol. Small amounts (of the order of 10%) of acetone, methyl ethyl ketone, normal and isoamyl alcohols can also be tolerated. However, butyraldehyde, butyric acid and its esters are not completely extracted from the benzene solutions, so that in their presence high results will be obtained for tertiary butanol. Hydrocarbons and halogen derivatives, which are not soluble in the recommended H_2SO_4-HCl acid mixture should be absent in the test samples.

Experimental Procedure. Into a test tube fitted with a close fitting ground-glass stopper, and which had been weighed on an analytical balance, was introduced an aliquot of test sample (0.2-0.5 g) and an aliquot of benzene (0.2-0.4 g); both sample and benzene were weighed accurately. During introduction of sample and benzene care should be taken to see that the stopper remains dry. 5 ml of a mixture of 37% hydrochloric acid and 80% sulfuric acid (2 : 1) * was then introduced, the stopper of the test tube was moistened with the mixture, the test tube was securely stoppered and then vigorously shaken for five minutes. After standing for a short time, a few drops of the upper layer were accurately withdrawn by means of a pipet fitted with a rubber cap and rapidly transferred to an Abbe-type refractometer. * *

Using the refractive index–coefficient K (schematically shown in the diagram) curve, the value of K corresponding to the refractive index measured is determined, and the tertiary butanol content calculated by means of the formula given above.

The working curve was constructed by treating several aliquots of benzene and tertiary butanol (or its concentrated aqueous solutions of known composition) with ratios of K up to 1.1 with the sulfuric–hydrochloric acid mixture under the conditions indicated above. Table 2 contains the experimental results obtained with tertiary butanol having a melting point of 24.8°, and used for constructing the working curve during checking of the method.

Results obtained on checking the method on complex mixtures of alcohol and water are given in Table 1.

SUMMARY

Tertiary butanol can be determined in the presence of the primary and secondary alcohols by selective conversion of the tertiary alcohol into its chloride, with subsequent measurement of the refractive index of a mixture of the tertiary chloride and an aliquot of benzene.

The experimental accuracy is ± 0.2-0.4% (absolute) on the average, while a determination takes about 20 minutes.

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* To prepare the acid mixture, sulfuric acid sp.gr. 1.84 was first diluted to a concentration of 80%, and, after cooling, twice its volume of concentrated hydrochloric acid was added to it carefully with stirring in a fume cupboard.

* * An IRF-22 refractometer was used in the work described here. The mixture should be transferred rapidly onto the refractometer prism, and the prism block closed immediately, since appreciable evaporation of the tertiary chloride can lead to low results for the tertiary butanol content.

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POLAROGRAPHIC DETERMINATION OF GLYOXILIC ACID

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Glyoxilic acid is obtained by the electrolytic reduction of oxalic acid in the presence of sulfuric acid. For its production control a method is necessary which would enable both glyoxilic and oxalic acids to be determined separately. At present, the method in use at the "Red Star" (Khar'kov) plant for the determination of glyoxilic acid is an iodometric method, which,however, is not selective,* and, accordingly, is not fully satisfactory for production control. We have developed a polarographic method for the determination of glyoxilic acid.

Glyoxilic acid is reduced on a dropping-mercury electrode [1, 2]. In acid solutions (KCl + HCl) $E_{1/2}$ for glyoxilic acid changes with pH, and at pH > 4.3 (KCl + HCl + KOH) a second wave appears for which $E_{1/2} =$ $= -1.32$ volt with respect to the normal calomel electrode, while the first wave disappears [2]. Reduction of glyoxilic acid has, however, not been studied in detail. There is no published information on the possibility of a quantitative polarographic determination of glyoxilic acid.

Experimental procedure and the results obtained. The polarographic work was carried out with a FG M-8 polarograph using a dropping-mercury electrode ($m = 0.954$ mg/sec, $t = 5.5$ sec at $E = 0$).

The glyoxilic acid was removed from the electrolyte after electrolysis of oxalic acid on lead electrodes. Separation of glyoxilic acid from oxalic and sulfuric acids was carried out by the action of excess $CaCO_3$. By this treatment oxalic and sulfuric acids were precipitated as their calcium salts, while calcium glyoxilate remained in solution. The solution obtained was filtered free from the precipitate through a filter paper, and an equal amount of ethanol was then added to it. During this stage of calcium glyoxilate was precipitated. This salt was recrystallized several times from alcohol and dissolved in water. The solution obtained was passed through a column of a cation exchange resin in the H^+ form. The column height was 50 cm, its diameter 10 mm, and the rate at which the solution issued out of the column was 0.3 ml per minute.

As detailed studies showed, glyoxilic acid is reduced on the dropping-mercury electrode forming polarographic waves, each of which corresponds to a definite state of the glyoxilic acid in solution or to a definite reduction mechanism.

In Fig. 1 are shown polarographic waves for glyoxilic acid in a buffer solution with a pH of 12.

Changes in the halfwave potentials as a function of the pH are shown in Fig. 2. The polarographic wave of glyoxilic acid is kinetic in character, in connection with which its wave height depends to a considerable extent on the temperature. The wave height changes by an average of 12.5% for each degree (within the temperature range 18-38°).

The nature of the change in wave height with pH is shown in Fig. 3, from which it is evident that at high glyoxilic acid concentrations polarograms should be taken at a pH of 4-6, while at low concentrations the polarograms should be taken at pH 11.5-12.5.

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*Formaldehyde and other aldehydes may be formed in addition to glyoxilic acid during electrolysis of oxalic acid.

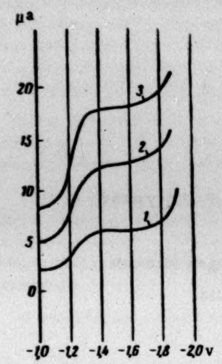

Fig. 1. Polarographic waves for glyoxilic acid in a supporting electrolyte of a buffer solution with a pH of 12. 1) c = 1.95 mM/liter; 2) c = 3.9 mM/liter; 3) c = 5.85 mM/liter.

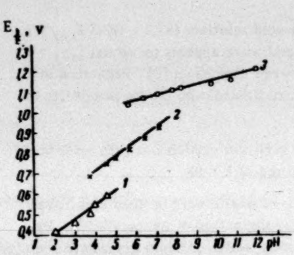

Fig. 2. Relation between the halfwave potential ($E_{1/2}$) of glyoxilic acid and pH.

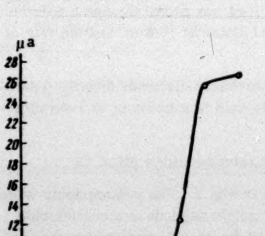

Fig. 3. Relation between the diffusion current (I_d) of glyoxilic acid and pH.

The wave height of glyoxilic acid is proportional to its concentration (Fig. 4).

The results obtained enabled us to use a polarographic method for the quantitative determination of glyoxilic acid in solution. For this purpose 0.5-1 ml of a solution of glyoxilic acid with a concentration of 1-2% was placed in an electrolytic cell and buffer solution added in such amount that the total volume of the mixture was 10 ml; polarograms were taken after passing hydrogen through the solution for 5-10 minutes to mix it and to remove dissolved oxygen.

The amount of glyoxilic acid was determined by means of a calibration line constructed by taking polarograms of glyoxilic acid solutions of known concentration, or by the method of additions.

Determination of glyoxilic acid and oxalic acid. As is evident from the polarograms shown in Figs. 5 and 6, addition of oxalic acid does not affect the wave height of glyoxilic acid; additions of glyoxilic acid do not affect either $E_{1/2}$ (- 1.8 to -1.9 volt with respect to the saturated calomel electrode) or the wave height of oxalic acid. This means that is is possible to determine glyoxilic and oxalic acids in each other's presence.

In order to check on this possibility the following synthetic mixtures of glyoxilic and oxalic acids (the glyoxilic acid concentration was 0.1075 M, while the oxalic concentration was 0.1 M) were prepared:

Glyoxilic acid (%)	20	40	50	60	80
Oxalic acid (%)	80	60	50	40	20

The mixtures were neutralized with 0.2 $(C_2H_5)_4NOH$ to a rose color with respect to phenolphthalein, and polarograms were taken for each mixture, first in a supporting electrolyte of a buffer solution with a pH of 12 (determination of glyoxilic acid), and then in a supporting electrolyte of 1 N $MgCl_2$ (determination of oxalic acid [3]). For the determination of glyoxilic acid, 0.5 ml of mixture (containing more than 50% of the acid) and 4.5 ml of supporting electrolyte, or 1 ml of mixture and 4 ml of supporting electrolyte (for acid contents of 50% and less in the mixture) were placed in the electrolytic cell. The galvanometer of sensitivity used for taking the polarograms was S = 1 : 50 of its maximum sensitivity. For the determination of oxalic acid, 0.5 ml of supporting electrolyte (1 N $MgCl_2$) and 0.5 ml of mixture were placed in the electrolytic cell and polarograms taken at a sensitivity of S = 1 : 100. On the basis of the wave heights obtained, and using the calibration curves, the concentrations of the acids were determined after taking into account the dilution which occurs on neutralization. The results obtained are given in the table.

Taken, g-eq/ liter		Found by the polarographic method, g-eq/ liter		Relative error, %	
glyoxilic acid	oxalic acid	glyoxilic acid	oxalic acid	glyoxilic acid	oxalic acid
0,0215	0,0800	0,0200	0,0790	—6,9	—0,8
0,0430	0,0600	0,0420	0,0620	—4,7	+3,3
0,0537	0,0500	0,0505	0,0520	—5,9	+4,0
0,0645	0,0400	0,0614	0,0430	—4,8	—7,5
0,0860	0,0200	0,0855	0,0195	—0,58	+2,5

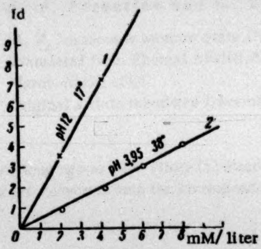

Fig. 4. Calibration lines for glyoxilic acid in a supporting electrolyte of buffer solutions. 1) pH 12, t = = 17°; 2) pH 3.95, t = 38°.

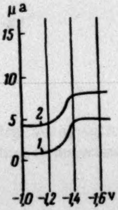

Fig. 5. Polarographic waves for glyoxylic acid in a supporting electrolyte of a buffer solution with a pH of 12, in the presence of oxalic acid. Glyoxylic acid concentration c = 2.10 mM/liter. 1) In the absence of oxalic acid; 2) with the addition of oxalic acid (c = 0.70 mM/liter)

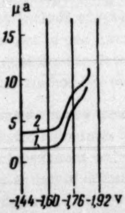

Fig. 6. Polarographic waves for oxalic acid in a supporting electrolyte of 1 N $MgCl_2$, in the presence of glyoxilic acid. Oxalic acid concentration c = 1.46 mM/liter. 1) In the absence of glyoxilic acid; 2) with the addition of glyoxilic acid (c = 2.1 mM/liter)

In two solutions, 0.350 and 0.175 M of glyoxilic acid were found by the polarographic method, and 0.360 and 0.180 M, respectively, by iodometric methods.

The following procedure is recommended for the analysis of production solutions. Ten ml of the production solution, which is a solution of a mixture of sulfuric, glyoxilic, and oxalic acids is placed in a 100 ml standard flask, neutralized to the rose color of phenolphthalein with tetraalkylammonium hydroxide, and diluted to the mark with water. An aliquot of the solution obtained is placed in the electrolytic cell to which is added 1 N magnesium chloride, and after the mixture has been purged with a stream of hydrogen, polarograms are taken of oxalic acid.

An aliquot of the solution which has been neutralized beforehand is also taken for determination of glyoxilic acid, buffer solution with a pH of about 12 is added, and after purging with hydrogen and establishing the temperature at the requisite level, polarograms of glyoxilic acid are taken. The concentrations of the two acids are determined by means of the calibration curves or by the method of additions.

SUMMARY

A polarographic method has been developed for the determination of glyoxilic acid in its mixtures with oxalic acid in production solutions.

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PHOTOMETRIC DETERMINATION OF CYCLOHEXANONE OXIME IN THE PRESENCE OF CAPROLACTAM

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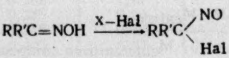
As long ago as 1898 Piloty [1] discovered that by the action of certain halogenizing agents, aliphatic oximes are converted into the corresponding gem-halonitroso compounds according to the scheme:

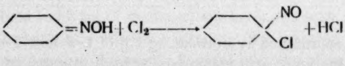


$$RR'C{=}NOH \xrightarrow{X-Hal} RR'C\begin{matrix} NO \\ Hal \end{matrix}$$

Piloty and other authors have prepared a large number of such halonitroso compounds, derivatives of both ketoximes and aldoximes. Most of the liquid materials have an intensely blue or blue-green color; their formation has been used as a qualitative reaction for oximes [2].

A number of halogenizing agents have been suggested for the preparation of gem-halonitroso compounds from oximes; they include nitrosyl chloride [3], hypobromites and hypochlorites [4, 5], halogenimides [6, 7], and free halogens, but not in one instance has it been possible to get stable yields, and this has prevented the use of this reaction for quantitative determination of oximes. Thus, Wichterle [6] tried to use chlorourea for halogenation; however, this method has not been widely used since the color obtained is not stable.

We have found that by treating with gaseous chlorine at room temperature, in the absence and the presence of solvents, aliphatic ketoximes are quantitatively converted into gem-halonitroso compounds. Our first test material was cyclohexanone oxime which is an intermediate in the industrial synthesis of caprolactam. It was found that by the action of chlorine, cyclohexanone oxide is quantitatively converted into 1-chloro-1-nitrosocyclohexane, first described by Rheinboldt [8]:



1-Chloro-1-nitrosocyclohexane is readily soluble in most organic solvents. We have established that the optical density of its solutions conforms to Beer's law, while its absorption spectrum in the visible region (Fig. 1) is characterized by an absorption maximum at 650 mμ; this coincides with published results [8].

The work was carried out on a standard SF-4 spectrophotometer and on a FÉK-M industrial photocolorimeter with a KS-14 light filter having maximum transmission at 640-750 mμ.

The reaction which was used for preparing the gem-chloronitroso compound in our modification could be used for the reliable qualitative and quantitative determination of aliphatic ketoximes and some other classes of oximes. Within the limits of the completeness of the oximation reaction of the ketones, our method could also be used for the photometric determination of ketones.

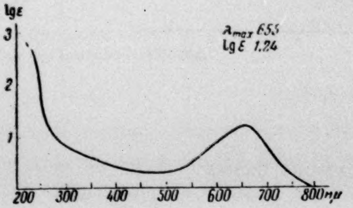


Fig. 1.

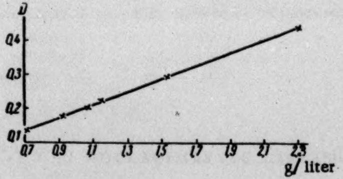


Fig. 2.

For series determination of cyclohexanone oxime on a FÉK-M apparatus, the following technique can be used: an aliquot of the test material, containing 0.1-0.2 g of oxime, is dissolved in 50 ml of methanol and a stream of technical chlorine passed through the solution for five minutes at the rate of two drops a second through a tube with a diameter of 5 mm. At the same time 50 ml of methanol is saturated with chlorine to serve as a reference solvent.

When the test solution has been saturated with chlorine it is transferred to a 100 ml standard flask and the volume made up to the mark with methanol. A 2 cm cell of the photocolorimeter is filled with the solution; a similar cell is filled with the methanol saturated with chlorine. The optical density is determined using a KS-14 filter. The oxime concentration of the test solution is determined by means of the formula:

$$C = \frac{D \cdot M_{\text{oxime}}}{k \cdot L \cdot M_{\text{chloronitroso compound}}}$$

where C is the oxime concentration in g/liter, L is the thickness of the absorbing layer in cm, k is the absorption coefficient in g/liter, and M is the molecular weight.

For cyclohexanone oxime M = 113.2, while for 1-chloro-1-nitroso-cyclohexane M = 147.6; k in methanol is 0.096. Substituting the values calculated we get

$$C = 7.99\,\frac{D}{L} \tag{1}$$

1-Chloro-1-nitrosocyclohexane is prepared by passing a slow stream of chlorine through a flask, containing 10 g of cyclohexanone oxime, cooled on a water bath, until the solid phase disappears. Excess chlorine does not lead to the formation of by-products. The blue liquid formed is distilled under vacuum, the fraction distilling at 52°/12 mm being collected. Yield 12 8 g (98%), d_4^{20} 1.1136; n_D^{20} 1.4630.

The absorption curve of 1-chloro-1-nitrosocyclohexane in the ultraviolet and the visible is shown in Fig. 1. Determination was carried out in a SF-4 spectrophotometer using a 0.1 M solution of chloronitrosocyclohexane in methanol, and a layer thickness of 1 cm in the range 200-300 mμ, and a 0.01 M solution in the range 500-700 mμ.

The absorption coefficient was determined by introducing 1 g of 1-chloro-1-nitrosocyclohexane into a 100 ml standard flask and diluting to the mark with methanol. Several solutions of varying concentrations (see Table 1) were prepared from the standard solution prepared in this way. Measurements were carried out on a FÉK-M apparatus using a layer thickness of 2.01 cm. The concentration and the absorption coefficient k = = D/C · L were calculated in g/liter. The mean value of the absorption coefficient determined from more than 20 experiments was 0.096. The relation between dilution and optical density is shown graphically in Fig. 2.

In order to establish the stability of 1-chloro-1-nitrosocyclohexane solutions in methanol, the standard solution was kept in the dark for 7 days, and then diluted and photometric measurements carried out The results obtained are given in Table 1. Within the limits of experimental error, the optical density of the solutions did not change on standing.

TABLE 1

1-Chloro-1-nitrosocyclohex hexane concentration, g/liter	Optical density		Extinction coefficient
	fresh solution	solution after 7 days	
2,3114	0,440	0,442	0,095
1,5400	0,296	0,296	0,096
1,1550	0,228	0,228	0,098
1,0710	0,206	0,205	0,096
0,9240	0,181	0,181	0,097
0,7140	0,137	0,137	0,095
0,5355	0,103	0,102	0,096

TABLE 2

Oxime taken, g/liter	Optical density, D	Oxime found, g/liter	Relative error, %
1,58	0,405	1,61	+1,5
1,35	0,346	1,37	+1,5
1,18	0,301	1,19	+1,0
1,05	0,269	1,07	+1,5
0,95	0,238	0,94	—0,2
0,87	0,218	0,86	—0,3
0,79	0,195	0,77	—2,3

TABLE 3

Oxime taken, g/liter	Caprolactam concentration, g/liter	Optical density, D	Oxime found, g/liter	Relative error, %
1,527	1,8	0,383	1,52	—0,4
1,311	1,5	0,330	1,31	—0,4
1,146	1,4	0,287	1,14	—0,3
1,932	8,2	0,485	1,92	—0,3
1,932	12,3	0,484	1,90	—1,5
1,932	16,4	0,486	1,91	—1,1

Determination of Cyclohexanone Oxime in a Reaction Mixture with Excess Chlorine. From 2 to 5 g of cyclohexanone oxime was dissolved in 50 ml of methanol and saturated with chlorine for 10 minutes. In another flask methanol was chlorinated to serve as a reference solvent. The reaction mixture was transferred to a 100 ml standard flask and diluted with methanol to the mark. Several solutions of varying concentrations were prepared from the solution obtained. The results of the measurements which were carried out on a FÉK-M photometer with a KS-14 filter, and with an absorbing layer 2.01 cm thick, are given in Table 2. The values given in column 3 were were calculated by means of formula (1).

Determination of Cyclohexanone Oxime in the Presence of Caprolactam. Several solutions containing a mixture of cyclohexanone oxime and caprolactam in known concentrations were prepared. Each of these solutions was saturated with chlorine, diluted to 100 ml methanol, and then photometrically measured as described above (see Table 3) The values of the oxime concentration given in column 4 were calculated by means of formula (1). The sensitivity of the FÉK-M apparatus permits determinations to be carried out in a 2 cm cell at concentrations not less than 2×10^{-1} g/liter. Oxime determination can be carried out directly in the reaction mixture after the Beckman rearrangement. This fact opens up the possibility of using this method for the direct control of the industrial process.

SUMMARY

1-Chloro-1-nitrosocyclohexane is quantitatively formed by the action of gaseous chlorine on cyclohexanone oxime (in the pure form or in solution). Solutions of 1-chloro-1-nitrosocyclohexane in methanol conform to Beer's law. On the basis of the observations made, a method has been developed for the photometric determination of cyclohexanoneoxime in its mixtures with caprolactam. The accuracy of the method is within the limits of 2% of the oxime content.

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BRIEF COMMUNICATIONS

THE DETERMINATION OF TRITIUM

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In studies connected with labelled hydrogen, it is convenient to use the radioactive hydrogen isotope tritium. Considerable work has been devoted to the determination of tritium by means of a Geiger-Muller counter, after conversion of the tritium to the gaseous state. However, in a number of cases it is desirable to determine tritium in the form of water vapor, which excludes the difficult operation of converting the tritium from water into hydrogen. The possibility of such a determination of tritium has been pointed out in the literature [1-2].

A schematic diagram of the setup is shown in Fig 1. The technique of analyzing water vapor permits determination of small amounts of tritium (0.0002 k/liter). Fig. 2 shows that on adding small amounts of the vapor of ordinary water (up to 3 mm), the plateau of the counter does not change appreciably. SBM-7 industrial-type metallic counters filled internally were used. Isopentane at a pressure of 16-18 mm was used as the filling gas When isopentane is used, difficulties arise as a result of the fact that it dissolves the vacuum grease. Accordingly, it was found necessary to use a tap with a special shape which is shown in Fig. 3. The upper part of the tap was greased with the usual vacuum grease; the lower part, which is separated from the top part by a groove sharpened into a stopper, being lubricated with a grease based on mannite. For reading low water-vapor pressures a butyl phthalate manometer was used (Fig. 4).

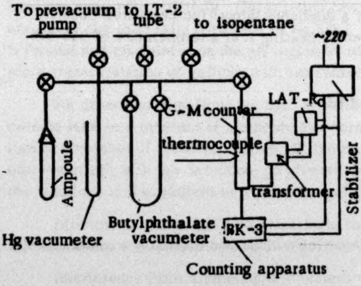

Fig. 1. Schematic diagram of the setup for determining tritium in the form of water vapor.

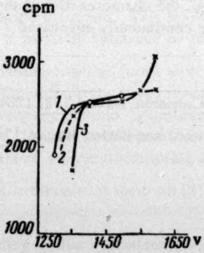

Fig. 2. Relation between the number of impulses per minute and the voltage applied to the counter. 1) 0 mm; 2) mm H_2O; 3) 8 mm.

During work with water vapors there is observed an appreciable change in the number of impulses in the counter with the course of time which is connected with the condensation on the counter walls.

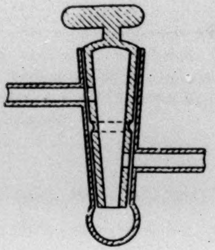

Fig. 3. Vacuum tap for isopentane.

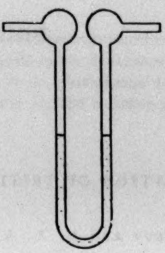

Fig. 4. Butyl phthalate manometer.

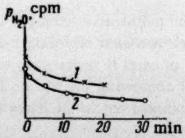

Fig. 5. The relation between the impulse number and the water vapor pressure and time. 1) Impulses/minute; 2) H_2O pressure.

In Fig. 5 is shown the change of the count with time, while in curve 2 the change of pressure with time is shown. Since the distribution of water vapor between the counter surface and the volume depends strongly on the temperature, the counter has to be thermostatted. In our setup the counter was heated to 30° by passing a current of 30 amp through the body of the counter. Thanks to the low thermal inertia of the counter the necessary temperature was readily established by means of a LATRa apparatus. The temperature was controlled by a thermocouple. For standardizing the readings of the water vapor pressure, the pressure was measured 5 minutes after letting in the sample. The sample was fed into the counter; the isopentane was then let in. The isopentane–water vapor was kept for 25 minutes, after which the activity was measured.

By standardizing all the procedures, the relative error was established at 7%.

It should be pointed out that the characteristics of the counter deteriorate strongly in the presence of small amounts of air as an impurity, and also after the passage of a discharge through the evacuated counter. After a discharge, the characteristics of the counter can be restored by heating it at a temperature of 250-300° while it is being continuously evacuated.

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DETECTION OF GALLIUM IN MATERIALS FROM ALUMINUM PRODUCTION

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Detection of small amounts of gallium in the presence of large amounts of aluminum is a difficult problem. Concentration of gallium contained in various materials in small amounts can be carried out by coprecipitating it with aluminum hydroxide. However, on separating gallium from objects containing small amounts of aluminum, it is better to use titanium hydroxide as a collector.

Gallium hydroxide is precipitated at pH 3 [1]. Titanium hydroxide starts to separate out from more acid solutions. In nitrate solutions, the pH value at which precipitation of titanium hydroxide starts is 1.4, while the pH at which coagulation commences is 1.65 [2]. Thus, towards the beginning of the formation of gallium hydroxide, the precipitate should be completely formed. Aluminum salts have a stabilizing action on titanium hydroxide The pH at which precipitation starts and the pH at which coagulation of titanium hydroxide commences are both higher when aluminum salts are present in the solution. Using a potentiometric titration method, we established that from a hydrochloric acid solution containing aluminum in an amount which is four times that of titanium (10 mg titanium and 40 mg aluminum), the pH at which titanium hydroxide starts to precipitate increases to 2.0, while commencement of coagulation is observed at pH 2.8. At a pH of 3.5, particles of coagulated precipitate appear. In the presence of 100 times its amount of aluminum, coagulation of the titanium becomes even more difficult. Coagulation can only be caused by addition of sulfate [in the form of a small amount of the solid salts $(NH_4)_2SO_4$ or Na_2SO_4]. Thus, in the presence of large amounts of aluminum, titanium is formed and coagulated in the pH region within which gallium hydroxide is formed. This leads to almost complete coprecipitation of gallium with titanium hydroxide. Aluminum is partially entrained by this precipitate.

For detection of gallium we used alizarin (1,2-dihydroxyanthraquinone), which forms with gallium a red-colored lake in a medium of ammonia and ammonium chloride [3]. The selectivity of the reaction is low. The ions of a number of elements, above all, those of elements which accompany gallium—aluminum, indium, zinc, etc.—interfere with the detection, to give red- and violet-colored lakes. In order to increase the selectivity of the reaction, it is expedient to extract the gallium alizarinate by means of a water-immiscible organic liquid.

Attempt to extract gallium alizarinate selectively by ether in an ammoniacal medium [3] was not successful: aluminum and indium behave like gallium.

Interference from aluminum and indium was removed by extracting gallium alizarinate with ethyl ether from an ammoniacal-oxalate buffer solution at pH 8-10. Under these conditions gallium forms an oxalate complex. The latter, as polarographic experiments we carried out [4] show, is not more stable than the corresponding ammine. The sensitivity of the detection of gallium in an ammoniacal-oxalate solution is not less than that in a solution containing ammonia and ammonium chloride.

In an ammoniacal-oxalate buffer, when there is a sufficient excess of ammonium oxalate, aluminum does not give a colored lake with alizarin. Indium, which forms an oxalate [5], does not interfere with gallium detection either.

***Deceased.**

Gallium alizarinate separates out in an ammoniacal-oxalate solution as a precipitate or a colloid. Because the precipitate is poorly wetted by water, on shaking with ethyl ether it collects in the form of a raspberry film on the phase boundary.

The sensitivity of the detection is 10^{-6} g in 1 ml of solution. In order to increase the sensitivity it is useful to add a readily soluble salt (e.g. NH_4Cl).

Detection of Gallium in Products and Intermediates from Aluminum Production. To the test hydrochloric acid solution is added a $TiCl_4$ solution (containing 10-20 mg titanium); ammonia (1 : 1) is added dropwise to the appearance of an appreciable turbidity, some dry $(NH_4)_2SO_4$ is then added to coagulate the precipitate. The precipitate, which is separated by filtration or centrifuging is treated with 3-4 ml of a 10% sodium hydroxide solution. The solution obtained is saturated with solid ammonium oxalate and the whole shaken vigorously for 1-2 minutes; a few drops of an alcoholic solution of alizarin and 1-2 ml of ethyl ether are finally added. After the mixture has been shaken and it has separated out completely into layers, when gallium is present the latter appears in the form of raspberry-red flocs or as a film on the boundary of the aqueous and organic solvent phases. When high concentrations of gallium are present, this film envelopes the ether layer and partially rises above it. Under such conditions the ether layer remains colorless. Separation into layers occurs rapidly when ether is used, but 1-2 drops of ethanol can be added to accelerate the separation. When a very bulky precipitate is obtained water is added.

It is useful to carry out a control test with a solution of an aluminum salt in order to check on the reagents. Sometimes, solutions of poorly purified alizarin which are not freshly prepared form a slight film on the interface of the phases on shaking with ether. Materials containing gallium are dissolved by the usual method.

About 1.0 g of test material should be taken for detecting gallium in aluminum or in its alloys.

The qualitative reaction suggested could serve an approximate quantitative evaluation from the point of view of limiting norms.

SUMMARY

For detecting gallium in materials from aluminum production, the former is separated by coprecipitating it on titanium hydroxide, and detecting gallium in the form of its alizarin lake, which is extracted from an ammoniacal-oxalate buffer solution with ethyl ether onto the interface of the phases. Indium and aluminum do not interfere.

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*Original Russian pagination. See C. B. Translation.

SEPARATION OF TITANIUM FROM TUNGSTEN BY ION EXCHANGE CHROMATOGRAPHY

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During the separation of titanium and tungsten by means of acid hydrolysis, the tungstic acid which settles out contains appreciable amounts of titanium. In order to separate these two elements we used SBS cation exchange resin in the hydrogen form, which has only slight reducing properties. Titanium is converted into the cationic form while tungsten remains in the anionic state The height of the cation exchange resin in the column was 300 mm and the diameter of the column was 15 mm.

Passage of normal solutions of a mixture of titanium sulfate and sodium tungstate through a column of SBS cation exchange resin did not lead to a sufficiently good separation. Under these conditions, not only was there observed complete absorption of titanium by the active groups of the resin, but some of the tungsten was also absorbed, presumably, in the form of tungstate (WO_2^{2+}) cations. Nevertheless, the main part of the tungsten appeared in the filtrate in the form of the anions (WO_4^{2-}).

Taken, mg		Obtained, mg	
titanium	tungsten	titanium	tungsten
2,58	2,12	2,55	2,16
2,58	0,52	2,55	0,53
2,55	2,34	2,58	2,33
1,59	2,50	1,57	2,52
1,59	5,00	1,55	5,05
0,52	2,25	0,53	2,25

In order to avoid absorption of tungsten by the cation exchange resin, the acidity of the solution was lowered to pH 5, and hydrogen peroxide added [1]. Under these conditions the tungsten was changed into pertungstic acid, while the titanium changed into the stable complex per-acid cation.

In order to avoid absorption, 5 ml of a 10% solution of hydrogen peroxide was added to 50 ml of a weakly acid test solution and ammonia then added until the pH was 5 (congo red). The solution prepared in this way was then passed through the column of cation exchange resin in the hydrogen form at the rate of 3-4 ml per minute. Under such conditions the titanium was quantitatively absorbed by the active groups of the resin, while all the tungsten passed into the filtrate. The titanium absorbed by the cation exchange resin was eluted with a 10% sulfuric acid solution (250 ml at the rate of 10 ml/minute). After the separation, the titanium was determined in the form of its compound with hydrogen peroxide by colorimetric titration. The filtrate, containing tungsten, was heated with sulfuric acid in order to destroy the hydrogen peroxide; the tungsten was reduced with titanium trichloride and determined by the thiocyanate method. The separation method gave satisfactory results (see Table).

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DETERMINATION OF METHYLOL GROUPS IN PHENOLIC RESINS

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Two methods are in current use in analytical laboratories for the determination of methylol groups—$-CH_2OH$. The first method [1] is based on the oxidation of methylol groups by iodine in an alkaline medium ($R\text{-}CH_2OH + I_2 + H_2O \rightarrow RH + HCOOH + 2HI$). This method of determining methylol groups cannot be used for the analysis of technical phenolic resins [2].

The second method is based on condensation of methylol containing compounds with phenol ($HOC_6H_4-CH_2OH + C_6H_5OH \rightarrow HOC_6H_4-CH_2-C_6H_4OH + H_2O$).

The methylol group content is established on the basis of the amount of water liberated, on the basis of the amount of phenol which reacts, or from the increase in weight of the resin after the condensation. Vansheidt [3] was the first to suggest phenol as a reagent for the determination of methylol groups. Subsequently, this method was described by a number of authors [4-7], the latter determined these groups on the basis of the amount of water liberated after condensation of the methylol-containing compounds with phenol [4-6], or with cresol [7]. Martin [4] measured the liberated water in a calibrated trap by azeotropic distillation with benzene. For accurate volumetric determination by Martin's method, large amounts of sample and reagent are necessary. The amount of phenol used up in each determination is 500-600 g. In addition a special distillation apparatus is necessary.

In more recent papers [5-7], the authors, while adhering to Martin's method, have suggested that the water liberated be determined by titration with Fischer reagent.

We tried to determine the content of methylol groups in phenolic resins by measuring the liberated water with Fischer reagent. However, the poor stability of the titrated solutions, the high sensitivity towards atmospheric moisture, the complexity of the apparatus, and also the fact that Fischer solution can only be used for colored solutions when an electrometric titration is carried out, led us to reject this method.

In subsequent investigations we determined the methylol groups on the basis of the amount of phenol which had reacted rather than on the basis of the water liberated. Essentially the method consists of condensing the methylol groups with excess phenol in the presence of hydrochloric acid. Having determined the amount of phenol used up in the reaction, it is possible to calculate the content of the methylol groups in the resin.

An aliquot of test resin (150-250 mg) was placed in a 150-200 ml round-bottom flask and 1 ml of an 80% aqueous solution of phenol added by pipet. The flask was connected to a reflux condenser and placed on a boiling water bath, 10 ml of 1 N hydrochloric acid was then introduced through the condenser. After two hours the flask was cooled and its contents carefully transferred to a special flask for steam distilling off the unreacted phenol.

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*Laboratory assistant G. N. Korzyukov helped in the experimental work.

Test material	CH_2OH content, %
Phenol alcohol No. 1	17.84-17.87
Phenol alcohol No. 2	27.8 -28.1
Resol resin (emulsion)	33.09-22.7
Dimethylolurea No. 1•	46.7 -46.4
Dimethylolurea No. 2•	45.9 -45.7
Trimethylolmelamine•	42.3 -42.8
Hexamethylolmelamine•	58.8 -58.4

•Technical product

The distillate was collected in a 1000 ml standard flask. Steam distillation was continued until the distillate gave no turbidity with bromine water. When distillation was complete, free phenol was determined by means of GOST-901-46

In parallel, a control steam distillation was carried out with the test resin to which 1 ml of the 80% aqueous solution of phenol had been added. By subtracting the amount of phenol in the distillate from the test material from the amount of phenol in the distillate from the control test, the amount of combined phenol is found, i.e., the phenol which has reacted with the methylol groups.

Assuming that one molecule of phenol reacts with one methylol group, the methylol content is calculated by means of the following formula:

$$x = \frac{(a-b)\,0.33}{c}$$

where $\underline{x}$ is the percentage content of methylol groups, $\underline{a}$ is the percentage content of phenol obtained in the control test, $\underline{b}$ is the percentage content of phenol in the test itself, and $\underline{c}$ is the weight of resin taken; 0.33 is the conversion factor.

It is also necessary to take into account the free phenol content of the resin itself as determined by GOST-901-46. In this case the formula used for the calculation will have the form:

$$x = \frac{a-(b-d)\cdot 0.33}{c}$$

where $\underline{d}$ is the content (in percent) of free phenol in the resin.

For the analysis of resins containing free formaldehyde, the percentage of methylol groups is calculated by means of the formula:

$$x = \frac{a-(b-d)\cdot 0.33}{c} - D$$

where D is the percentage of free formaldehyde in the resin.

We determined the methylol group content of the condensation products of phenol with formaldehyde, and also of urea and melamine methylol derivatives. Results with good reproducibility were obtained (see Table). During the determination of the methylol groups in pure o-hydroxybenzyl alcohol (saligenin) the following results were obtained 24.85, 25.19, and 24.90% of CH_2OH; the theoretical content is 25.0%.

Determination of free phenol and formaldehyde does not complicate the work when this technique is used, because it can be carried out in accordance with GOST requirements.

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THE EFFECT OF PARALDEHYDE ON THE PHOTOMETRIC DETERMINATION OF CROTONALDEHYDE

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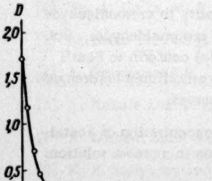
We tried to apply the photometric method of determining crotonaldehyde in the ultraviolet [1] to the analysis of the liquid products obtained by the catalytic conversion of acetaldehyde over a calcium-phosphate catalyst [2]. The deviations which were obtained between the results for crotonaldehyde by the photometric determination indicated, and by chemical analysis, led us to carry out a more detailed study of the liquid products from the catalytic condensation of acetaldehyde. In addition to crotonaldehyde, acetic acid, and acetaldehyde, these products were found to contain paraldehyde b.p. 121°; d_4^{20} 0.9900; n_D^{20} 1.4019. The published data for paraldehyde are: b.p 123.2-123.5°; d_4^{20} 0.9943; n_D^{20} 1.4049 [3]. Under the action of concentrated sulfuric acid, paraldehyde is converted completely into acetaldehyde (b.p. 21°) during distillation. Since we were interested, in the given instance, in the analysis of the products obtained, we set aside the question of how the paraldehyde is formed: whether it is formed from acetaldehyde under the influence of the catalyst—calcium phosphate, in a similar fashion to what is observed under the influence of sulfurous acid [4], concentrated sulfuric acid, hydrochloric acid, zinc chloride, $COCl_2$ [5], ethyl iodide, cyanogen [6],etc., or whether paraldehyde is the product of a secondary reaction—conversion of acetaldehyde under the action of the materials formed in the catalytic process.



Absorption curve of paraldehyde.

In the work described here we studied the effect of paraldehyde on the optical density of neutral aqueous solutions of crotonaldehyde, and also on the optical density of aqueous solutions of crotonaldehyde containing acetaldehyde. The results obtained supplement the technique for the photometric determination of crotonaldehyde in the ultraviolet [1].

First of all the absorption curve of pure paraldehyde (its characteristics are given above) was taken on a SF-4 spectrophotometer in a 0.1 mm quartz cell in the range 220-365 mμ (Fig. 1).

Subsequent work was carried out on a FM visual photometer adapted for operating in the ultraviolet [7] and using quartz plane-parallel cells with a thickness of 25 mm. The absorption curve of paraldehyde (Fig. 1) shows that it is possible to use this apparatus with a UFS-3 filter. The experimental procedure has been described before [1].

The following materials were used for preparing model mixtures:

Crotonaldehyde (obtained by dehydration of acetaldol with orthophosphoric acid) b.p. 101°, n_D^{20} 1.4364 Published data for crotonaldehyde b.p. 101.3-102.0°, n_D^{20} 1.4356 [8].

TABLE 1

Relation between Optical Density and the Concentration of Paraldehyde in an Ethanol Solution

Paraldehyde concentration, % (volume)	100	50	25	12.5	6.25	3.12
Optical density (D)	0.52	0.26	0.13	0.06	0.03	0.00

TABLE 2

Effect of Paraldehyde on the Optical Density of Crotonaldehyde Solutions

Crotonaldehyde, % (volume)	Paraldehyde, % (volume)	Optical density (D)
2,50	0,00; 0,50; 5,0; 8,0; 10,0	0,43; 0,46; 0,49; 0,51; 0,54
1,25	0,00; 0,25; 2,5; 4,0; 5,0	0,21; 0,22; 0,24; 0,26; 0,27
0,62	0,00; 0,12; 1,25; 2,0; 2,5	0,10; 0,11; 0,11; 0,13; 0,13
0,31	0,00; 0,06; 0,62; 1,0; 1,25	0,05; 0,05: 0,04; 0,06; 0,06
0,15	0,00; 0,03; 0,31; 0,5; 0,62	0,02; 0,00; 0,00; 0,03; 0,03

Paraldehyde (prepared by purification of the commercial material) b.p. 122-123.5°; d_4^{20} 0.9963; n_D^{20} 1.4037.

Acetaldehyde (obtained by depolymerization of paraldehyde in the presence of concentrated sulfuric acid) b.p. 21°; n_D^{20} 1.3318. Published data b.p. 21°, n_D^{20} 1.3316 [9].

Solutions of paraldehyde in ethanol conform to Beer's law (Table 1).

Quantitative determination of paraldehyde in ethanol solution is only possible on the photometer used when the paraldehyde concentrations are high enough [not less than 25% (by volume)]. The use of longer cells would, probably, permit determination of lower paraldehyde concentrations.

Since paraldehyde itself possess an insignificant density in dilute solutions, additions of this material will increase the optical density of aqueous solutions* of crotonaldehyde (Table 2) to a greater degree.

Thus, even small amounts [0.12-0.5% (volume)] of paraldehyde lead to an increase in the optical density of aqueous solutions of crotonaldehyde, as a result of which the curve relating optical density to crotonaldehyde concentration established earlier [1] cannot be used for the quantitative determination of crotonaldehyde. But, since aqueous solutions of crotonaldehyde (containing up to 10% by volume of paraldehyde) conform to Beer's law, the amount of crotonaldehyde can be calculated if the paraldehyde concentration is established beforehand. In such cases the results given in Table 2 permit construction of a family of calibration curves.

It is known [1] that for crotonaldehyde contents up to 1.6% (volume) the limiting concentration of acetaldehyde which will not affect the optical density of crotonaldehyde during its determination in aqueous solutions amounts to a maximum of 15% (volume).

Actual aqueous condensates obtained during catalytic experiments on the conversion of acetaldehyde [2] contained 2.5 and 0.5% (volume) of crotonaldehyde and 15 and 25% (volume) of acetaldehyde, respectively. The effect of acetaldehyde on the optical density of crotonaldehyde was determined by using synthetic mixtures of the same composition as the aqueous condensates given above. It was established that these solutions conform to Beer's law (Table 3), although the curve relating optical density to crotonaldehyde concentration for these solutions is somewhat higher than the calibration curve for crotonaldehyde alone [1]. In Table 3 is shown the effect of paraldehyde on the optical density of aqueous solutions of crotonaldehyde containing acetaldehyde.

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*Water and ethanol are optically transparent within the limits of the ultraviolet part of the spectrum used in this case.

TABLE 3

Effect of Paraldehyde on the Optical Density of Aqueous Solutions of Crotonaldehyde Containing Acetaldehyde

Crotonaldehyde, % (volume)	Acetaldehyde, % (volume)	Paraldehyde, % (volume)	Optical density (D)
0,50	25,0	0,00; 0,50; 5,0; 10,0	0,22; 0,26; 0,27; 0,32
0,25	12,5	0,00; 0,25; 2,5; 5,0	0,11; 0,13; 0,13; 0,13
0,12	6,25	0,00; 0,12; 1,25; 2,5	0,05; 0,06; 0,06; 0,06
0,06	3,12	0,00; 0,06; 0,62; 1,25	0,02; 0,03; 0,04; 0,03
0,03	1,56	0,00; 0,03; 0,31; 0,62	0,00; 0,00; 0,00; 0,00
2,50	15,0	0,00; 2,0; 5,0; 10,0	0,50; 0,60; 0,63; 0,93
1,25	7,5	0,00; 1,0; 2,5; 5,0	0,25; 0,30; 0,30; 0,31
0,62	3,75	0,00; 0,50; 1,25; 2,5	0,12; 0,15; 0,14; 0,15
0,31	1,88	0,00; 0,25; 0,62; 1,25	0,06; 0,07; 0,06; 0,07
0,15	0,94	0,00; 0,12; 0,31; 0,62	0,03; 0,03; 0,03; 0,04

As is evident from Table 3, additions of paraldehyde to aqueous solutions of crotonaldehyde containing acetaldehyde leads to an even greater increase in the optical density than is observed in solutions which do not contain acetaldehyde (see Table 2).

Additional experiments established that in aqueous solutions containing 0.5 and 2.5% (volume) of crotonaldehyde and 25-15% (volume) of acetaldehyde, respectively, the maximum paraldehyde concentration for which crotonaldehyde determination is still possible is 2.0% (volume). In these cases, therefore, calibration curves should be constructed on the basis of the results obtained for solutions of the composition indicated, free from paraldehyde.

SUMMARY

The photometric method for the determination of crotonaldehyde in the ultraviolet can be used for aqueous solutions containing paraldehyde and high contents of acetaldehyde. The limits of the applicability of the method have been established.

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THE PHOTOMETRIC DETERMINATION OF BARBITURIC AND 2-THIOBARBITURIC ACIDS

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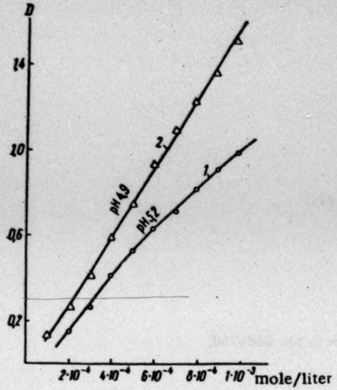
Brightly colored salts of violuric acid (or, what is the same, 5-isonitrosobarbituric acid) are formed by the interaction of barbituric acid and the nitrites of the alkali and alkaline earth metals, as Baeyer established [1]. A similar reaction for 2-thiobarbituric acid has been described by Isherwood [2]. Although the structure and some of the properties of the violurates and 2-thioviolurates have been studied by Hantzsch [3], Wagner [4], and Lal and Dutt [5], the conditions under which these salts are formed have not been established hitherto, and no attempts have been made to use the reactions indicated for the quantitative determination of barbituric and 2-thiobarbituric acids. This is connected with the fact that the colors are not stable enough under conditions where the pH is not controlled. Erlenmeyer and Schoenauer [6] and Erlenmeyer, Hahn, and Sorkin [7] came up against this difficulty when they tried to use violuric acid as a developer during the chromatographic separation of mixtures of the cations of the alkali and alkaline-earth metals [8].

We studied the interaction of barbituric and 2-thiobarbituric acids with nitrites in 0.01-0.001 M solutions [9], and established that the formation and stability of the characteristic colors of the violurates and 2-thioviolurates, respectively, depend not only on the temperature but also on the pH of the solution. The optimum pH for sodium and potassium violurates was found to be 5.0-5.2, while for sodium and potassium 2-thioviolurates the optimum pH was 4.7-4.9. Solutions of sodium violurate and 2-thioviolurate have absorption maxima at 520 and 570 mμ, respectively.

The colors formed gradually disappear on standing. At 100° and at the optimum pH and at pH values below this optimum value, the color of the violurate and 2-thioviolurate forms very rapidly, reaches a maximum in the first 10-15 minutes, and then gradually weakens. On the other hand, at pH values higher than the optimum value, only a comparatively slow increase in color is observed, and a maximum value is not achieved even at 100° for 60 minutes.

The results mentioned above were obtained both in experiments where a considerable excess of barbituric and 2-thiobarbituric acid, respectively, was used, and in experiments where excess nitrite was used in the reaction solution. In the latter case all the features noted were observed in the course of a comparatively limited time of interaction (about 10-15 minutes at 100° and many hours at 20°). During the longer interaction times of the nitrite gradual disappearance of the colors formed was observed.

The results which we obtained earlier [10] led us to use the reaction indicated for the quantitative determination of nitrite and to develop a photometric method using 2-thiobarbituric acid. In the present work described here, on the basis of the conditions found for the formation of colors by the interaction of barbituric and 2-thiobarbituric acids with excess nitrite, we have developed a method for the quantitative photometric determination of barbituric and 2-thiobarbituric acids.



Such a determination is, obviously, possible under conditions where the pH of the solution is strictly controlled, and best of all at the optimum pH. For this purpose we used a twofold excess by volume of a phosphate-citrate or acetate buffer mixture with a pH of 5.2 for the determination of barbituric acid, and with a pH of 4.9 for the determination of 2-thiobarbituric acid.

In all the experiments the reaction mixtures were heated at 100° for 15 minutes and then immediately cooled with ice water to 20°. The colors obtained in this way are stable enough at 20° (for several hours).

The curves shown in the figure give the results of our experiments in the form of a relationship between the optical density of the colors formed and the concentration of barbituric acid (Curve 1) and 2-thiobarbituric acid (Curve 2). In each experiment 13 ml of the citrate-phosphate or acetate buffer mixture was mixed with 5 ml of nitrite solution and 2 ml of barbituric acid or 2-thiobarbituric acid solution, respectively. The concentrations of the nitrite solution and of the respective solutions of the acids were the same so that in all the experiments the nitrite was in a 2.5 excess of the acids.

As is evident from the curves, the change in optical density of the 2-thioviolurate (Curve 2) with changes in the concentration of the original 2-thiobarbituric acid conforms fairly well to the Lambert-Beer law. In the case of barbituric acid (Curve 1) the color of the violurate which develops, although it does not strictly follow a linear relationship, does not deviate too much, and the curve obtained does permit the use of this method for quantitative purposes.

The results obtained show that photometric determination by this method is possible with an accuracy of not less than 5% if a standard curve is established beforehand. Such a determination is possible at a concentration as low as 10^{-4} M of barbituric or 2-thiobartituric acids, i.e., it is fairly sensitive. The cations of the alkali and alkaline earth metals do not interfere with the determination, since λ_{max} for their violurates, according to our observations, lies within the limits 510-530 mμ, while for the 2-thioviolurates their λ_{max} lies within the limits 570-580 mμ. Heavy metal cations (copper, iron) interfere with accurate determination.

SUMMARY

It has been found that the formation of colored violurates and 2-thioviolurates under certain conditions can be used for the quantitative photometric determination of barbituric and 2-thiobarbituric acids.

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LETTERS TO THE EDITOR

A LETTER TO THE EDITOR OF ZHURNAL ANALITICHESKOI KHIMII *

Received August 3, 1959

Dear Editor,

In the Journal of Analytical Chemistry, A. A. Nemodruk [1], so he assumes, has proved the worthlessness of the so-called hypothesis of the intermolecular dissociation of cyclic salts (IMD), on which I have worked for about 20 years. In this connection I should like to ask you to publish the following observations of mine.

It is generally accepted at present that organic salt and complexing agents form, at varying pH, so-called cyclic or chelate salts of varying composition with elements. Often several such salts may be present at the same time in solution, the ratio of the concentrations of these salts varying with pH changes. Some research workers assume that this change in the ratio of the concentrations may explain all those changes in the properties of solution of cyclic salts which occur on changing the pH.

After working for several years with solutions of cyclic salts I have come to the conclusion that such ideas are not enough to explain all the multiplicity of existing facts. The need has arisen to introduce some additional mechanisms, the development of which attracted me to the IMD hypothesis. In addition to my initial publications [2, 3], I have written about this hypothesis in subsequent articles [4-8] and have spoken considerably about it in my lectures on organic analytical reagents in Moscow and Leningrad .

The IMD hypothesis relates to the nature of those bonds by which the atom of the element is connected in cyclic salts with the residue of an organic reagent molecule. In general, these bonds are to a lesser or greater degree polar, or, as it is said, are to some extent ionic. The IMD hypothesis assumes that the degree of ionicity of these bonds does not remain constant, but changes with the pH of the medium, temperature, and other external factors. The IMD hypothesis assumes that a dissolved cyclic salt, even without changing its composition, can, with changes in pH, change its state, which is connected with changes in the degree of ionicity of the bonds of the atom of the element.

Acceptance of this basic proposition of the hypothesis permits a ready explanation of many facts which have hitherto not been explained satisfactorily. For example, it is known that the enhanced stability of cyclic salts to acidification can be explained by the fact that the increasing tendency of an atom of an element to change over on acidification of the solution to an unconnected ionic state is satisfied by a simple increase in the degree of IMD. In non-cyclic salts, however, on increasing the degree of ionic character of the atomic bond, there is a rapid decomposition of the salt. The IMD hypothesis explains the effect of pH on the color of solutions of cyclic salts [3] and permits one to make predictions, which is always worth-while, about the reactivity of cyclic salts, explains the structure of certain cyclic salts which various formulas cannot cover ([5] p. 189), and many others. The hypothesis is particularly useful for disclosing new color reactions and new methods of organic synthesis, for which it is even now an inexhaustible source of new discoveries.

The use of this hypothesis in the work of Russian and foreign research workers is continuously increasing (e.g. [9-11]). Recently, this hypothesis has started to interest physicists. In one of his papers on proton magnetic resonance, A. I. Rivkind states: "The latter fact is useful for the experimental study of the phenomenon of

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* Note on correction. A. A. Nemodruk's article has also been discussed by Yu. Bankovskii and A. Ievin'sh (Izv. Akad. Nauk. Latv. SSR, 12, 171 (1959).

intermolecular dissociation of complexes, theoretically predicted by V. I. Kuznetsov. It has been found that the intermolecular ionic state is a widely distributed property of complex particles . . . " [12], see also [13].

Returning to Nemodruk's article, we should point out that the first part of this article (pp 260-262, Figs. 1-3) proves, in Nemodruk's opinion, the worthlessness of the IMD hypothesis, by the fact that solutions of cyclic salts and solutions of the sum of the ionized and nonionized state of a reagent which are similar in color, have dissimilar light absorption curves.

Here Nemodruk misleads the reader by distorting the idea behind a technique which is useful in simple cases for getting an approximate evaluation of the extent of IMD ([2], p. 813), and sets forth in a distorted form the essence of the hypothesis. IMD essentially assumes that cyclic salts with IMD possess properties which are intermediate between the properties of the ionized and nonionized state of a reagent, and are, at the same time, individual compounds,and not mixtures. Accordingly, it is completely incomprehensible on what basis Nemodruk makes such a conclusion (p. 262, line 8 from the bottom): "The absence in solutions of complex salts of both the ionic and undissociated forms of a reagent, is incompatible with the idea of the intermolecular dissociation of these salts, developed by Kuznetsov [2, 3]".

Nemodruk misleads the reader even more by placing conclusions I made long ago after his conclusions, by writing at the beginning of the article (p. 260, line 5 from the bottom): "we have established a number of factors which are incommensurable with the hypothesis of IMD. What one should understand by this "we" is obvious from the following comparisons.

My article (1950)

([3] p. 818, line 3 from the bottom) " . . . . the absorption curves of solutions of cyclic salts are similar in appearance to the absorption curves of both forms of the reagent and lie between them (Fig. 1, see also 15, 16, 22). The absorption curves of the sum of the colors of the different forms of the reagent differ strongly from the absorption curves of solutions of cyclic salts (Fig. 2), and it is only as a result of the capacity of the eye to sum the colors that the physiological impression of the identity of these colors arises.

Nemodruk's article (1959)

(p. 262, middle of the page) "With respect to their absorption curves, these complexes occupy an intermediate position between the undissociated enols and their ionic state." (p. 261, line 2 from the bottom) "Thus, from a comparison of the light absorption curves of solutions of complexes and of solutions of the reagents, which coincide in color, it follows, that . . . in the case of solutions of complexes . . . a new form, intermediate between the dissociated and undissociated forms,appears."

Accordingly, in the first part of his article, Nemodruk adds to the diagram which I gave ([3], p. 819, Fig. 2) yet another three such diagrams, repeats in different words conclusions which I had already made, misleads the reader by distorting the essence of the hypothesis, and then writes his conclusion regarding the "worthlessness" of the IMD hypothesis!

The rest of Nemodruk's article has been constructed on the same principle. For the sake of brevity I shall limit myself to some examples.

(In p. 268 Nemodruk reproaches me for the fact that I (for brevity) in the formula for the symmetrical gallium salt of pyrocatechol depicted IMD on one bond only. Nemodruk emphasizes that IMD should be manifested along both bonds. All this is true, and credit should be given to him, if this fact had not already been pointed out by me earlier. Here is a comparison.

> **My article (1952)**
>
> ([4] p. 179, line 2 from the bottom) "In the symmetrical structure of a complex the ionic state of the bonds is distributed evenly between both bonds."
>
> **Nemodruk's article (1959)**
>
> (p. 268, middle of the page) "If then these groups are completely identical, as for example in the case of the cyclic gallium salts of pyrocatechol . . ., the assumption of the unequal value of the two completely similar bonds . . ., made by Kuznetsov . . . cannot be justified by any means."

Having "unmasked" the IMD hypothesis by this method, Nemodruk sets up in opposition to it polarization hypotheses, the application of which, in the case under consideration, he is inclined to regard as his own. Nemodruk writes that the IMD hypothesis is "erroneous in its basis propositions, it can only show a negative effect. . . . it should be replaced . . . . by polarization hypotheses" (p. 270). What then is the difference between IMD and the hypothesis regarding the degree of ionic character of a bond or, as Nemodruk prefers, polarization hypotheses? They are one and the same, the only difference is in the terms used.

At the beginning of the present letter I advanced some ideas regarding the enhanced stability of cyclic salts. One might not agree with these ideas, one can dispute them. But such refutations must be backed by evidence; one cannot write, as Nemodruk does, "intermolecular dissociation cannot be linked up with the high stability of cyclic salts". Discussing the reactivity of cyclic salts (p. 266), Nemodruk cites more recent work in which he participated, without referring to my earlier publications in which he did not participate. This "usurpation" of my priority occurs in other places.

Nemodruk's article is unfortunate in other respects. His article abounds in mistakes and testifies to his lack of understanding of the essence of the IMD hypothesis. Thus, on p. 266, discussing (incidentally, very erroneously) the reasons for the colors of solid materials, Nemodruk writes ". . . in the solid state, in which, as is known, no ordinary or intermolecular dissociation takes place." Consequently, according to Nemodruk, ionic crystals do not exist in nature. Developing "his" polarization theories, in p. 269, Nemodruk gives, what in his opinion is useful, the example of the colors of the potassium and sodium nitrophenolates: K–red, Na–yellow. Actually, only the aqueous (with 2 H_2O) sodium nitrophenolate is yellow, while the anhydrous material is red [14].

I can only express regret that the editorial board of the Journal of Analytical Chemistry did not give me the opportunity to become acquainted with Nemodruk's article prior to its publication.

V. I. Kuznetsov

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CHRONICLE

CONFERENCE ON PHASE (MATERIAL) ANALYSIS OF NONFERROUS METAL ORES, THEIR ENRICHMENT PRODUCTS, AND PRODUCTS OF THEIR METALLURGICAL TREATMENT

(July 10-15, 1959, Ordzhonikidze)
Translated from Zhurnal Analiticheskoi Khimii, Vol. 15, No. 2, pp. 253, March-April, 1960

The conference on phase (material) analysis was convened by the Scientific-Technical Society of Nonferrous Metallurgy, the State Scientific-Research Institute of Nonferrous Metals ("Gintsvetmet") and the Council of Social Economy of the Northern Osetinskii Economic Administrative Territory. Twenty-five enterprises and 26 scientific institutions took part in the work of the conference. Twenty-one reports and 16 communications were read on the analysis of ores, their enrichment products, and their metallurgical processing products for compounds of the following elements: Cu, Pb, Zn, Cd, Mo, W, Sn, Be, Ta, Al, Ti, Fe and Si.

The conference acknowledges that in contrast to ores and their enrichment products, for which analytical methods have been developed for the compounds of a number of elements, the products of metallurgical processing (slags, matte, annealing products, dust) have not been at all satisfactorily studied, while development of techniques for their analysis has proceeded slowly. A successful and fairly complete study of the material composition of such products is only possible under such conditions, where in addition to using chemical methods based on selective solution, use is also made of mineral-petrographic, x-ray structural, thermal, local x-ray spectrographic and other methods of analysis.

The conference noted the following papers (as the most interesting ones): "Separate determination in ores of finely dispersed copper oxide combined with the components of interfering rock" (Gintsvetmet); "Chemico-mineralogical study of agglomerates obtained from oxidized nickel ores" (Mekhanobr); "Determination of the forms of molybdenum in molybdenum—tungsten ores and their enrichment products, with separate determination of molybdenum of the crystalline lattice of scheelite" (Gintsvetmet); "Determination of oxygen compounds in the matte from lead melts" (Vniitsvetmet); "Determination of the various forms of tungsten in ores with separate determination of tungsten, scheelite, hubnerite, and wolframite" (Gintsvetmet); "Analysis of lead compounds in industrial accumulators" (NIAI branch); The use of oxidation inhibitors for the analysis of products containing metallic phases in addition to oxides and salts (Gintsvetmet); "Mineralogical (phase) composition of slags from lead water-jacket melts" (Vniitsvetmet) and others.

The conference noted: the absence of a modern textbook on phase analysis (the book by V. V. Dolivo-Dobrovol'skii and Yu. V. Klimenko was published in 1947 and does not contain methods for the analysis of metallurgical processing products); insufficient training of analytical chemists in universities; the absence of coordination of such work. The insufficient amount of work published and the delay in publishing papers were also noted; the absence of the requisite apparatus was pointed out.

The conference pointed out the main directions along which phase analysis should develop. We shall only deal with some of them: studies of the composition of metallurgical slags, matte, annealing products, and dusts; a comparative study of the properties, in particular, of the solubility of natural minerals and their synthetic analogs; the use of oxidation inhibitors for metallic and sulfide phases; the development of rapid methods.

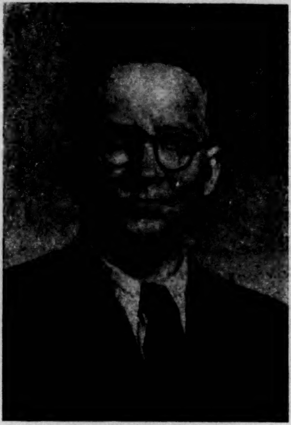
The conference has placed before the Ministry of Higher and Secondary Education the question of introducing into universities and mining—metallurgical higher education institutions, a course on the "Theory and Practice of Chemical Phase (Material) Analysis".

The conference accepted a resolution to create at the Gintsvetmet Institute a commission to coordinate the work on phase analysis in nonferrous metallurgy; to advise the State Planning Committee of the USSR to expand the production of the necessary apparatus, and to intercede with the Central Direction of Scientific-Technical Society about the publication of the papers given at the conference, and to organize zonal seminars for workers in laboratories.

It was decided to convene a second branch conference in 1962.

OBITUARY

SERGEI KUZ'MICH CHIRKOV



SERGEI KUZ'MICH CHIRKOV
February 21, 1900 - May 28, 1959

On May 28, 1959, the death occurred, after a serious illness, of Sergei Kuz'mich Chirkov, a doctor of chemical sciences, a professor, and the head of the chair of analytical chemistry in the Ural State University.

Sergei Kuz'mich was born on February 21, 1900 in Glazov. In 1913 he finished at his first school, but because of financial reasons, he did not have the chance to study further and worked as a messenger and then as an apprentice mechanic. While working, Sergei Kuz'mich carried on with his own education, and, in 1923 he entered Perm University where he finished in 1927; after this he worked as an assistant and then carried out the duties of a reader in the Perm Chemicotechnological Institute.

In 1933, S. K. Chirkov went to Sverdlovsk where he worked in the Ural Branch of the Academy of Sciences of the USSR as a senior chemist and as head of the laboratory. From 1937 Sergei Kuz'mich worked as senior engineer—as a research worker in a dichromate factory and from 1939 he worked in the Sverdlovsk Scientific Research Hygiene Institute where he was head of the hydrochemical and physicochemical laboratory, and carried out the duties of the director of the institute. In 1946, S. K. Chirkov defended his Doctor's thesis, and was confirmed in his post as professor in 1948.

Since 1951 S. K. Chirkov has been the head of the chair of analytical chemistry in the Ural University, where he worked to the end of his life. While working there he devoted a great deal of his energy to improving teaching, educational, and scientific research work. His lectures were very popular with his students and with his co-workers in the faculty.

S. K. Chirkov made great demands on himself, his co-workers, and his students. Under his direction many of his students prepared and defended their candidates' theses.

Having a broad scientific background and a great capacity for work, Chirkov was for a long time a scientific consultant to the Ural Geological Administration, to the chemical laboratory of the Institute of Ferrous Metals, and other institutions.

Sergei Kuz'mich Chirkov was an outstanding Soviet scientist. He published 72 scientific papers and more than 35 papers in the form of manuscripts are located in the libraries of scientific research institutions and institutes. Chirkov carried out a great deal of work on obtaining salts from the wastes of chemical production, on the study of equilibrium systems on the crystallization of isomorphous mixtures, on questions of the extraction and distribution of bromide and iodide in alkali halide systems, on glass technology, on the study of the composition of ores, on the rational composition of chromite charges, and so forth. He published a large amount of work on analytical chemistry in the field of titrimetric methods of analysis, and on electrometric, polarographic, and photometric methods.

Many of the methods developed by S. K. Chirkov have been introduced into practice.

The memory of S. K. Chirkov will remain forever in the hearts of all those who knew him.

The Commission on Analytical Chemistry of the Academy
of Sciences, USSR
Ural State University

NEW BOOKS

PUBLICATIONS OF THE ACADEMY OF SCIENCES OF THE USSR WHICH ARE TO BE PUBLISHED IN 1960

Translated from Zhurnal Analiticheskoi Khimii, Vol. 15, No. 2, pp 255-256
March-April, 1960

For the information of readers of this journal about books which are ready to be published, starting with the present issue, information will be given about books on chemistry which the Academy of Sciences, USSR Press, intends to publish in 1960. Other journals of the Academy of Sciences Press will contain information on books relating to the subjects dealt with in those journals.

The list given below can be used for making preliminary orders for these books.

The books should be ordered by letter from the office most convenient to the buyer; a list of these offices are given at the end of this list. When the books have been published they will be sent out COD.

T. D. Avtokratova, Analytical Chemistry of Ruthenium, V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, 15 sheets, 11 rubles.

Analysis of Gases and Metals, (Trans. Commission on Anal. Chem. Vol. XV, V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry) 17 sheets, 12 rubles.

The collection contains articles on various questions relating to the analysis of gases in metals; the theoretical bases of analysis, various analytical methods (vacuum fusion, spectrographic, x-ray structural, thermo-fractional, isotopic, chemical, etc.) and analytical apparatus.

G. V. Bykov, The History of the Classical Theory of Chemical Structure. The Institute of the History of Natural Sciences and Technics, Academy of Sciences, USSR, 19.5sheets, 15 rubles.

G. V. Bykov, The Electronic Charges of Bonds in Organic Compounds. Chem. Sciences Division, Academy of Sciences, USSR, 11 sheets, 8 rubles.

O. V. Vershkovskaya, V. S. Krasnova, and V. S. Saltykova, Gallium, Methods of Study, Distribution in Rocks and Minerals, Types of Deposits. Institute of Mineralogy, Geochemistry, and Crystallochemistry of the Rare Elements, Academy of Sciences, USSR, 8 sheets, 6 rubles.

Problems in Geochemistry, Vol. II, Trans. Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Academy of Sciences, USSR, No. 46, 8.5 sheets, 6 rubles.

The collection contains articles on the distribution of scandium in minerals, the distribution of molybdenum in Central Asian rocks, and formation of hydrothermal solutions in rocks.

Hydrochemical Materials. Vol. 31. Hydrochemical Institute, Academy of Sciences, USSR, 15 sheets, 11 rubles.

The collection is devoted to various questions on the study of atmospheric, surface, underground, and mineral waters, and also to the chemical analysis of natural waters.

M. G. Gonikberg, Chemical Equilibrium and Reaction Rates at High Pressures. Institute of Organic Chemistry, Academy of Sciences, 14 sheets, 10 rubles.

N. V. Grum-Grzhimailo, Chemical Bonds in Metal Alloys 7.5 sheets, 5 rubles 50 kopecks.

Dislocation in Crystals. Bibliographical Index. 11 sheets, 6 rubles.

The index contains references to monographs, collections, reviews, and articles on this subject published in the period 1934-1958.

V. Ya. Eremenko, Spectrographic Determination of Microelements in Natural Waters. Hydrochemical Institute, Academy of Sciences, USSR, 5 sheets, 3 rubles 50 kopecks.

G. S. Kolesnikov, Synthesis of Vinyl Derivatives of Aromatic and Heterocyclic Compounds. Institute of Heteroorganic Compounds, Academy of Sciences, USSR, 23 sheets, 18 rubles.

V. É. Levenson, Geological Bituminology and Its Problems, Vol. I, Institute of Geology and Development of Fuels, Academy of Sciences, USSR, 17 sheets, 12 rubles.

N. P. Lisovskaya and N. B. Livanova, Chemistry and Metabolism of Phosphoproteins. A. N. Bakh Institute of Biochemistry, Academy of Sciences, USSR, 6 sheets, 4 rubles 50 kopecks.

S. V. L'vov, Some Questions in the Fractionation of Binary and Multicomponent Mixtures. Scientific-Technical Council on the Chemical Treatment of Petroleum Hydrocarbons, Academy of Sciences, USSR, 10 sheets, 7 rubles.

L. S. Mayants, Theory and Calculations of Molecular Vibrations, Institute of Heteroorganic Compounds, Academy of Sciences, USSR, 30 sheets, 23 rubles.

Methods for the Determination of Impurities in Pure Metals. Trans. Commission on Analytical Chemistry. Vol. XII. V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, 27 sheets, 21 rubles.

V. I. Mikheeva, The Hydrides of the Transitional Elements. N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, USSR, 13 sheets, 9 rubles.

Organic Reagents in Analytical Chemistry. Trans. Commission on Analytical Chemistry. Vol. XIV V. I Vernadskii Institute of Geology and Analytical Chemistry, Academy of Sciences, USSR, 25 sheets, 19 rubles.

The articles in this collection consider the relation between the structure of organic reagents and their analytical action, methods for the determination of individual elements are described, and the application of organic reagents is discussed in detail.

K. A. Osipov, Questions in the Theory of the Thermal Stability of Metals and Alloys. A. A. Baikov Institute of Metallurgy, Academy of Sciences, 18 sheets, 13 rubles.

F. M. Perel'man, Rubidium and Cesium. N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, USSR, 10 sheets, 7 rubles.

Underground Treatment of Fuel. Trans. Institute of Fuel. Academy of Sciences, USSR, Vol. XIII, 15 sheets, 11 rubles.

The following questions are discussed in this volume: the interaction of coal with carbon oxides, with hydrogen and with steam; underground gasification of coal and shale in canals using a steam-oxygen blast; gasification under high pressure; conditions for the igneous filtration cross sectioning of wells, etc.

E. V. Posokhov, Essays on the Hydrochemistry of Underground Water in the Central Zones of Kazakhstan. Hydrochemical Institute of the USSR, 12 sheets, 9 rubles.

E. A. Robinzon, Tatarskii ASSR Petroleum. Institute of Petroleum Chemical Synthesis. A. E. Arbuzov Chemical Institute, Academy of Sciences, USSR, 16 sheets, 11 rubles 20 kopecks.

N. M. Rodigina and É. N. Rodigina, Successive Chemical Reactions (mathematical analysis and calculations). Institute of Metal Physics, Academy of Sciences, USSR, 6 sheets, 4 rubles 50 kopecks.

Yu. I. Solov'ev, and O. E. Zvyagintsev, Nikolai Semenovich Kurnakov, His Life and Work. N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, USSR, 15 sheets, 11 rubles.

Thallium. (Basic Features of its Geochemistry, Mineralogy, Genetic Types of Deposits and Geochemical Provinces). Institute of Mineralogy, Geochemistry, and Crystallochemistry of the Rare Elements, Academy of Sciences, USSR, 10 sheets, 7 rubles.

Trans. Institute of the History of Natural Sciences and Technics, Academy of Sciences, USSR, Vol. 30, 20 sheets, 14 rubles. The collection includes discussions on the development of the various branches of organic chemistry, the history of the detection of niobium and tantalum, development of the theory of solutions, the study of the fixation of atmospheric nitrogen, the life and scientific and social work of outstanding scientists–chemists.

Trans. Institute of Oceanology, Academy of Sciences, USSR, Vol. 42. Problems in the Chemistry of the Sea. 18 sheets, 13 rubles.

The book is a collection of papers on various questions in the chemistry of the Okhotskii, White and Black Seas.

Trans. Marine Hydrophysical Institute, Academy of Sciences, USSR, Vol. XIX. Chemistry of the Sea. Hydrology. Geology of the Sea. 10 sheets, 7 rubles.

The collection contains papers on the questions of the chemistry of the sea, hydrology, and geology of the sea; results of the determination of organic carbon in the water of the North Eastern Atlantic are given.

R. B. Khesin-Lur'e, The Biochemistry of Cytoplasm. Institute of Biophysics, Academy of Sciences, USSR, 20 sheets, 14 rubles.

The Chemistry and Technology of Fuel. Trans. Institute of Fuel, Academy of Sciences, USSR, Vol. XII, 22.5 sheets, 17 rubles.

The collection includes results of the study of the properties of coal during oxidation; achievements in the technology of coke making, in the use of liquid and gaseous fuels are included; underground gasification of fuel is considered.

Chemistry of the Rare Elements. Bibliographic Index of Russian and Foreign Literature. No. 1. Section of Special Libraries,Network and Chemical Sciences Section of the Academy of Sciences, USSR, 54 sheets, 29 rubles.

Chromatography, Theory and Application. No. 2. Institute of Physical Chemistry, Academy of Sciences, USSR, 10 sheets, 7 rubles.

A collection of papers on various questions in ion exchange, complex formation, molecular, partition, and gas chromatography.

A. I. Shatenshtein, Isotopic Exchange and the Substitution of Hydrogen in Organic Compounds. Chemical Sciences Division, Academy of Sciences, USSR, 22 sheets, 17 rubles.

V. Ya. Shtern, Mechanism of the Oxidation of Hydrocarbons in the Gaseous Phase. Institute of Petroleum-chemical Synthesis, Academy of Sciences, USSR, 40 sheets, 30 rubles.

All orders for these books should be sent to the following address:

Moskva, Tsentr. B. Cherkasskii Per., 2/10
Kontora "Akademkniga", Otdel "Kniga-Pochtoi"
or to the nearest "Akademkniga" book shop.

Addresses of "Akademkniga" book shops.
Moskva, ul. Gor'kova, 6 (magazin No. 1); Moskva, 1-i Akademicheskii
Proezd, 55/5 (magazin No. 2); Leningrad, Liteinyi Prospekt, 57;
Sverdlovsk, ul. Belinskovo, 71-v; Kiev, ul. Lenina, 42; Khar'kov,
Goryainovskii per., 4/5; Alma-Ata, ul.Furmanova, 129; Tashkent,
ul. Karla Marksa; Baku, ul. Dzhaparidze, 13.

"Akademkniga"

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

At the Twentieth Conference of the Union of Pure and Applied Chemistry (Munich, August, 1959) the Committee of the Analytical Chemistry Division discussed some questions relating to terminology about which there is some confusion in the chemical literature.

As a result, the following recommendations were made:

1. Designations of Indicator in Titrimetric Analysis

A large number of dyes have been suggested as indicators in chelatometric and oxidation—reduction titrations, but a large number of trade names have been assigned to the same compounds. Instances have cropped up where a compound is recommended as a new indicator merely because it has another name, while in fact this compound had already been in use for many years.

In order to avoid further confusion and difficulties in writing edited articles, the Committee recommends the following: when a dye is used as an indicator, whatever the type of titration, particularly when the dye is recommended as a new one, in addition to the trade name of the dye, its British Color Index, or its number in the Shulz Table* should be given.

2. Terminology of Complexing Reagents

Because of the confusion which exists in the terminology of complexing agents used as standard solutions, the Committee recommends adoption of the following terms:

a) The group of polyamino-polycarboxylic acids which form anionic complexes, should be called "complexanes".

b) Titration methods which involve the use of solutions of complexing agents of any type should be called "complexometric titration".

c) Complexometric titrations which are carried out with solutions of chelate-forming reagents should be called "chelatometric titration". The latter is one of the forms of complexometric titration.

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* The Commission on Analytical Chemistry has asked the Institute of Scientific-Technical Information, Academy of Sciences, USSR to issue photostat copies of the British Color Index.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

DETERMINATION OF STABILITY CONSTANTS DURING STEPWISE COMPLEX FORMATION

N. P. Komar'
A. M. Gor'kii Kharkov State University

Translated from Zhurnal Analiticheskoi Khimii, Vol. 15, No. 3, pp. 260-263
May-June, 1960
Original article submitted April 16, 1959

The following polynominal equations have been suggested for determination of the stability constant (β_n) during stepwise complex formation [1, 2]

$$\frac{\Phi - 1}{ba} = \sum_{n-1}^{N} a^{n-1} \beta_n \text{ and } \frac{A - a}{B(1 - \bar{n})a} = \sum_{n-1}^{N} \frac{(n - \bar{n})}{(1 - \bar{n})} a^{n-1} \beta_n , \tag{1}$$

where $\Phi = B/b$ is Leder's "complexity", $\bar{n} = (A-a)B^{-1}$ is Bjerrum's "formation constant", $B = c_B$, $b = [B]$, $A = c_A$, $a = [A]$, N is the coordination number, and $\beta_n = [BA_n]b^{-1}a^{-n}$ at constant ionic strength. The values of B and A are always known; N is determined by the position of B in the periodic system and is controlled by the maximum value $\bar{n}$. Measurement of b and a is not always possible, but it has been shown [3, 4] that a, and this means also $\bar{n}$, can be calculated for any solution when the pH, B, and A are known, if the addendum is the anion of a weak acid, and if the system does not contain multinuclear and proton-containing complexes. All these conclusions have been reached, however, without taking into consideration hydrolysis of the B ion, and should be subjected to a check already carried out [5] for systems with one complex.

For studying stepwise complex formation, $c_{HR} = c_{H^+} = R$ or MOH $= c_{OH} = M$ is added to a system containing $c_{BR_\mu} = c_{B^{\mu+}} = B$ and $c_{M\nu A} = c_{A^{\nu-}} = A$. In the first instance $[A^{\nu-}] = a$ decreases, while in the second case it increases, leading to corresponding changes in the yield of complex, in the hydrolysis products $B^{\mu+}$ and $A^{\nu-}$ ions, and in the values of Φ and $\bar{n}$.

In the most general case, during a study of such systems it is necessary to take into account μ, the equilibrium of the stepwise hydrolysis of the $B^{\mu+}$ ion

$$B^{\mu+} + iH_2O \rightleftarrows B(OH)_i^{(\mu-i)+} + iH^+, \ [B(OH)_i^{(\mu-i)+}] = \eta_i b h^{-i}, \ h = [H^+]; \tag{2}$$

Q is the equilibrium of the hydrolysis of the same $B^{\mu+}$ ion, leading to the formation of nuclear chain hydrocomplexes [6]

$$\begin{gathered}(q+1)B^{\mu+} + qp\,H_2O \rightleftarrows B((OH)_pB)_q^{\{(q+1)\mu-qp\}+} + qpH^+; \\ \left[B((OH)_pB)_q{}^{\{(q+1)\mu-qp\}+}\right] = k_0 k^q b^{q+1} h^{-qp},\end{gathered} \tag{3}$$

where k_0k^q is the constant of the qth stage of the multichain hydrolysis; ν is the equilibrium of the association of the $A^{\nu-}$ ions with H^+ ions

$$A^{\nu-} + jH^+ \rightleftarrows H_jA^{(\nu-j)-}; \ [H_jA^{(\nu-j)-}] = \sigma_j h^j a, \tag{4}$$

where $\sigma_j = (K_{\nu-j+1} \ldots K_{\nu-1} K_\nu)^{-1}$ and $K_1, K_2, \ldots, K_\nu$ are the dissociation constants of a weak acid $H_\nu A$ in the first, second, and subsequent stages, and N is the equilibrium of stepwise complex formation

$$B^{\mu+} + nA^{\nu-} \rightleftarrows BA_n^{(n\nu-\mu)-}; \ [BA_n^{(n\nu-\mu)-}] = \beta_n b a^n. \tag{5}$$

Using the equations for the law of mass action (2)–(5), it is possible to write two material balance equations:

$$B=\varphi_1 b+k_0\sum_{q=1}^{Q}(q+1)k^q b^{q+1}h^{-qp}+b\sum_{n=1}^{N}\beta_n a^n,\ \varphi_1=1+\sum_{i=1}^{\mu}\eta_i h^{-i}; \tag{6}$$

$$A=\varphi_2 a+b\sum_{n=1}^{N}n\beta_n a^n;\ \varphi_2=1+\sum_{j=1}^{\nu}\sigma_j h^j \tag{7}$$

and the electroneutrality equation; in the case of addition of a strong acid HR this is of the form

$$\left.\begin{aligned}&\nu A+h+b\left[\mu+\sum_{i=1}^{\mu-1}(\mu-i)\eta_i h^{-i}\right]+\\&+k_0\sum_{q=1}^{Q}\{(q+1)\mu-qp\}k^q b^{q+1}h^{-qp}=\\&=\mu B+R+[\mathrm{OH}^-]+a\left[\nu+\sum_{j=1}^{\nu-1}(\nu-j)\sigma_j h^j\right]+\\&+b\sum_{n=1}^{N}(n\nu-\mu)\beta_n a^n,\end{aligned}\right\} \tag{8}$$

and is, in the case of addition of a strong base MOH,

$$\left.\begin{aligned}&\nu A+M+h+b\left[\mu+\sum_{i=1}^{\mu-1}(\mu-i)\eta_i h^{-i}\right]+\\&+k_0\sum_{q=1}^{Q}\{(q+1)\mu-qp.\}k^q b^{q+1}h^{-qp}=\\&=\mu B+[\mathrm{OH}^-]+a\left[\nu+\sum_{j=1}^{\nu-1}(\nu-j)\sigma_j h^j\right]+\\&+b\sum_{n=1}^{N}(n\nu-\mu)\beta_n a^n,\end{aligned}\right\} \tag{9}$$

where $[R^-]=c_{R^-}=\mu B+R$ and $[M^+]=c_{M^+}=\nu A$ in equation (8) and $[R^-]=c_{R^-}=\mu B$ and $[M^+]=c_M=\nu A+M$ in equation (9).

From (6) it follows that in the general case Leder's formula [1] will have the form

$$[\Phi-\varphi_1-f(b)]a^{-1}=\sum_{n=1}^{N}\beta_n a^{n-1}. \tag{10}$$

Bjerrum's formula [2] for the most general case is derived by dividing the value of $A-\varphi_2 a$ from (7) by N from (6)

$$\frac{\overline{n}_0[\varphi_1+f(b)]}{(1-\overline{n}_0)a}=\sum_{n=1}^{N}\frac{(n-n_0)}{(1-\overline{n}_0)}a^{n-1}\beta_n, \tag{11}$$

where $f(b)=k_0\sum_{q=1}^{Q}(q+1)k^q b^q h^{-qp}$, as in (10) and $\overline{n}_0=(A-\varphi_2 a)B^{-1}$ Accordingly, when nuclear-chain complexes are present, it is necessary to know $\underline{a}$ and $\underline{b}$ in order to calculate β_n, whichever equation is used.

When the concentrations of nuclear-chain complexes can be disregarded, the left-hand side of (10) acquires the form $(\Phi-\varphi_1)a^{-1}$, i.e., it remains a function of $\underline{b}$ and $\underline{a}$, since $\Phi=Bb^{-1}$; at the same time the left-hand side of equation (11) is converted into the expression $\overline{n}_0\varphi_1[(1-\overline{n}_0)a]^{-1}$ and for calculating the values of β_n by means of equation (11) it is sufficient to know a. Obviously, where it is possible to measure or calculate a directly, equation (11) acquires special interest. It should be emphasized that equation (10) is converted into Leder's general equation only for systems where it is possible to disregard the hydrolysis of $B^{\mu+}$ ions, while (11) changes into Bjerrum's equation only in those exceptionally rare cases where it is possible to disregard simultaneously the hydrolysis of both the metallo ion and the addendum.

In order to establish the possibility of calculating the values of a and b, equation (7) is multiplied by ν and equation (6) multiplied by μ is subtracted from it, it is then found that

$$b\sum_{n=1}^{N}(n\nu-\mu)\beta_n a^n = \nu A - \nu\varphi_2 a - \mu B + \mu\varphi_1 b + k_0\sum_{q-1}^{Q}(q+1)\mu k^q b^{q+1} h^{-qp} \tag{12}$$

Substitution of this value in equations (8) and (9), taking into account the values of φ_1 and φ_2, leads, after the usual transformations, to the equations

$$\psi_2 a + h = R + [\mathrm{OH^-}] + \psi_1 b + k_0\sum_{q-1}^{Q} qp.\, k^q b^{q+1} h^{-qp.}, \tag{13}$$

$$M + h + \psi_2 a = [\mathrm{OH^-}] + \psi_1 b + k_0\sum_{q-1}^{Q} qp.k^q b^{q+1} h^{-qp.}, \tag{14}$$

where

$$\psi_1 = \sum_{i-1}^{\mu} i\eta_i h^{-i}\ \text{и}\ \psi_2 = \sum_{j-1}^{\nu} j\sigma_j h^j. \tag{15}$$

Both of the calculating equations are of the (q + 1)-th degree with respect to b and are linear with respect to a; this means that it is necessary to know b in order to calculate a, while in order to calculate b, a must be measured beforehand. Thus, in the general case, one cannot do without measurements of the equilibrium concentrations, as has been thought hitherto [3, 4]. It is obvious that when nuclear-chain complexes are present one has to measure b and calculate a by means of the formulas

$$\left.\begin{aligned} a &= (\psi_1 b + k_0\sum_{q-1}^{Q} qp.k^q b^{q+1} h^{-qp.} + R + [\mathrm{OH^-}] - h)\,\psi_2^{-1}.\\ a &= (\psi_1 b + k_0\sum_{q-1}^{a} qp.\, k^q b^{q+1} h^{-qp.} - M + [\mathrm{OH^-}] - h)\,\psi_2^{-1}.\end{aligned}\right\} \tag{16}$$

When the system does not contain nuclear-chain complexes, equations (13) and (14) are readily reduced to formulas which can be used for calculation

$$\left.\begin{aligned} a &= (\psi_1 b + R + [\mathrm{OH^-}] - h)\,\psi_2^{-1},\ a = (\psi_1 b - M + [\mathrm{OH^-}] - h)\,\psi_2^{-1},\\ b &= (\psi_2 a - R - [\mathrm{OH^-}] + h)\,\psi_1^{-1},\ b = (\psi_2 a + M - [\mathrm{OH^-}] + h)\,\psi_1^{-1},\end{aligned}\right\} \tag{17}$$

from which it follows that in the case of simultaneous stepwise hydrolysis of both ions, b must be known to calculate a, and vice versa. Only in those cases when only one of the ions hydrolyzes, e.g., $A^{\nu-}$, can its concentration be calculated by means of the formulas

$$a = (R + [\mathrm{OH^-}] - h)\,\psi_2^{-1} \quad \text{or} \quad a = ([\mathrm{OH^-}] - M - h)\,\psi_2^{-1}. \tag{18}$$

Only Bjerrum's equation should be used in this case for determining the constant β_n, since in order to calculate the values of b on the basis of the values of a it would be necessary to use graphical integration [4].

When only $B^{\mu+}$ ions hydrolyze, then

$$b = (h - R - [\mathrm{OH^-}])\,\psi_1^{-1},\quad b = (h + M - [\mathrm{OH^-}])\,\psi_1^{-1}, \tag{19}$$

while the values of a must be measured since they enter into both Leder's and Bjerrum's equations.

Graphical methods [1, 2, 4, 7-9] have been mainly used for solving Leder's and Bjerrum's equations with respect to the value of β_n. It has been established that the values obtained for the constants are not very accurate, since the extrapolation and limiting conversions were carried out in the sphere of observation, where the experimental errors are particularly large and the errors accumulate in the values of the constants determined in the later stages of the solution. Successive-approximation methods suggested by some authors are also open to criticism [10], since the values thus obtained have proved to be not the sought for constants of the law of mass action, but only coefficients of one of the many possible interpolation formulas.

The only rational method of solving the system of equations (10) and (11) is a variant of the method of least squares, adapted for obtaining the most probable values of physical constants [11]. Their accuracy can then be checked at any given confidence level by means of the methods described by Krylov [12] and Romanovskii [13]. The appearance of values for the constants, which are statistically indistinguishable from zero, can be regarded as proof that the concentrations of the appropriate particles are negligibly small.

SUMMARY

It has been shown that by studying the possibilities of determining the constants of stepwise complex formation by the interaction of hydrolyzed metal ions and addenda, in the vast majority of cases direct measurements of the activities of the metal ion and the addendum are necessary. Formulas which can be used for calculation are given, and conditions have been established which permit some simplifications to be made.

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THE RELATION BETWEEN THE RADIATION INTENSITY AND CONCENTRATION OF 18 ELEMENTS IN THE FLAME-PHOTOMETRIC METHOD OF ANALYSIS

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Establishment of the relation between the radiation intensity I and the concentration C of an element in solution is of great importance for choosing the operating concentration range in flame-photometric analysis. Theoretically [1-4], the shape of the curves expressing this relation between I and C is determined by the self-absorption of the light in the flame, which depends on the value of the absorption parameter a–the ratio of the Lorentz and Doppler halfwidths of the spectral line being photometrically measured; $a = \Delta\nu_L/\Delta\nu D$. For low partial pressures of the atoms in the flame, the radiation intensity is directly proportional to the concentration. As the partial pressure of the atoms increases, as a result of self-absorption, the radiation intensity in the center of the line approaches the luminosity of an absolutely black body at the temperature of the flame and at the given wavelength, and becomes constant. Further increases in the radiation intensity measured by the photometer occur as the result of a Lorentz broadening of the spectral line. For values of the absorption parameter $a > 1$ the radiation intensity is proportional to the square root of the concentration C. For values of $a < 1$, there occurs an additional intermediate region, in which the radiation intensity hardly changes at all with concentration. In the logarithmic form the curves relating I and C are lines which in the initial region have a slope of unity ($I = KC$, $\lg I = \lg C + \lg K$; K is the proportionality constant); in regions of higher concentration the slope is equal to 0.5 ($I = KC^{\frac{1}{2}}$, $\lg I = \frac{1}{2}\lg C + \lg K$), for values of $a < 1$, in the intermediate concentration region, the lines have slopes less than 0.5 [$I = KC^b$, $\lg I = b \lg C + \lg K$, $b < 0.5$ (Fig. 1)].

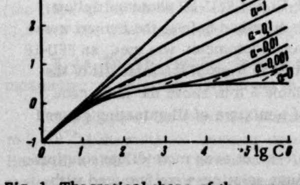

Fig. 1. Theoretical shape of the curves relating radiation intensity I to concentration C on a logarithmic scale, for various values of the absorption parameter [2].

In order to achieve the highest accuracy it is desirable that the determinations should be made in the region where the relation between radiation intensity and concentration is linear. In actual practice, however, the flame-photometric method may produce additional distortions of the shape of the curves relating I and C. In particular, when dealing with the alkali metals with low ionization potentials, and when hot flames are used, ionization becomes considerable. This leads to replacement of the metal atoms by ions, which do not radiate a line which can be measured photometrically. As a result, with decreasing C a rapid drop is observed in the radiation intensity, and the latter becomes proportional to the square root of the concentration.

In order to establish the possible distortions in the shape of the I vs C curves, we set ourselves the task of determining their shapes in the widest possible concentration

TABLE 1

List of Test Elements

Element	Compound	Wavelength, mμ		Concentration range studied, M
		line	molecular band peak	
Copper	Nitrate	324,7	—	$1—10^{-4}$
	"	327,5	—	$1—10^{-4}$
Silver	Nitrate	328,1	—	$1—10^{-4}$
	"	338,1	—	$1—10^{-4}$
Magnesium	Chloride	285,2	371,0	$1—10^{-4}$
	"	—	383,0	$1—10^{-4}$
Calcium	Chloride	422,7	554,0	$1—10^{-4}$
	"	—	622,0	$1—10^{-4}$
Strontium	Nitrate	460,7	680,0	$1—10^{-4}$
Barium	Chloride	553,5	870,0	$1—10^{-4}$
Yttrium	Chloride	—	615,0	$1—2\cdot10^{-5}$
Lanthanum	"	—	794,0	$1—10^{-4}$
Europium	"	459,2	—	$2\cdot10^{-2}—10^{-5}$
Ytterbium	"	398,8	—	$2\cdot10^{-2}—5\cdot10^{-5}$
Gallium	Chloride	403,3	—	$10^{-1}—10^{-4}$
	"	417,2	—	$10^{-1}—10^{-4}$
Indium	Chloride	451,2	—	$10^{-1}—10^{-1}$
Thallium	Sulfate	377,5	—	$2\cdot10^{-1}—10^{-4}$
		535,0	—	$2\cdot10^{-1}—10^{-4}$
Chromium	Chromic acid	425,4	—	$1—10^{-4}$
Manganese	Sulfate	403	—	$1—2\cdot10^{-5}$
Iron	Chloride	385,6	—	$1—10^{-3}$
		373,3	—	$1—10^{-3}$
Cobalt	Nitrate	352,5	—	$1—10^{-3}$
		345,1	—	$1—10^{-3}$
Nickel	Nitrate	352,5	—	$1—10^{-3}$
		341,5	—	$1—10^{-3}$

TABLE 2

Changes in the Slope of the Curve Relating the Intensity of the Ytterbium Line at 398.8 mμ to Concentration

Lowest value $\lg C$ ($\lg C_m$)	$\bar{2},0$	$\bar{3},7$	$\bar{3},3$	$\bar{3},0$	$\bar{4},7$	$\bar{4},3$	$\bar{4},0$	$\bar{5},7$
$\operatorname{tg}\alpha$	0,733	0,815	1,12	1,26	1,41	1,38	1,58	1,94

range for all elements that may be determined by flame-photometric methods, except the alkali metals, for which this had been done earlier [5].

EXPERIMENTAL TECHNIQUE

The apparatus described before was used [5-7]. Measurements in the visible and in the infrared were made by means of a spectrophotometer based on a UM-2 type monochromator, FÉU-19 and FÉU-22 photomultipliers, and a mirror galvanometer. The atomizer and atomizing chamber have been described before; the burners were glass. For measurements in the ultraviolet the monochromator of the SF-4 spectrophotometer was used, an FÉU-18 photomultiplier being attached to the output of the latter. The burner was fitted in front of the inlet slit of the monochromator in such a way that the radiation from the central part of the flame 5 mm above the inner cone fell on the slit. The flames of a mixture of acetylene and air (2360°K) and of a mixture of illuminating gas and air (1973°K) were used.

The experimental work consisted in preparing stock 1 M, or less often 0.1 M, or even more dilute solutions of the metal salt; then, by dilution of these stock solution, a series of more dilute solutions were prepared with concentrations 0.5, 0.2, and 0.1 of the original. These solutions were introduced in succession into the flame, and the photocurrent readings were expressed as a percentage of the photocurrent of the original solution. Curves relating log photocurrent readings to log concentration were constructed. A list of the metals studied, together with the wavelengths used or the peaks of the molecular bands, is given in Table 1. The lower concentration limit for an element was determined by the sensitivity of the method, and was related to the ratio of the intensity of the radiation being measured photometrically to the value of the flame background for a given wavelength.

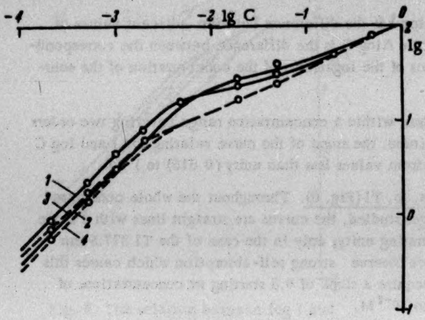

Fig. 2. Relation between log I and log C for the Cu lines 324.7 mμ (1) and 327.5 mμ (2), and for the Ag lines 328.1 mμ (3) and 338.1 mμ (4).

RESULTS

Cu, Ag. The surves relating the line intensity and the concentration of these elements, drawn on a logarithmic scale, are given in Fig. 2.

It is clear from Fig. 2 that the shape of the curves obtained corresponds to that predicted theoretically for the case where the absorption parameter a lies between 1.0 and 0.1. The regions in which the slope of the straight line is equal to 1 is only observed for a concentration range of 10^{-4} to $2 \cdot 10^{-3}$ M; above this concentration the slope of the line is about 0.3 for copper and about 0.4 for silver, i.e., the radiation intensity becomes proportional to the cube root of the concentration in the case of copper and $\sqrt[2.5]{C}$ in the case of silver. At higher concentrations of these elements, the slope of the line becomes 0.5, and the radiation intensity becomes proportional to the square root of the concentration C. The curves obtained with an illuminating gas flame almost coincide with those obtained with an acetylene flame; it was possible, however, to follow them up to metal concentrations of 10^{-3}M.

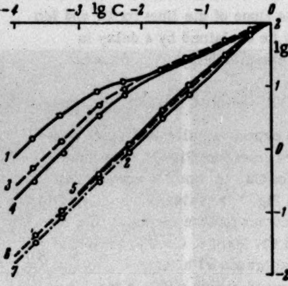

Fig. 3. Relation between log I and log C for Mg 285.2 mμ(1), MgOH 371 and 383 mμ (2), Ca 422.7 mμ (3), Sr 460.7 mμ (4), Ba 553.5 mμ (5), CaOH 622 mμ (6), SrOH 680 mμ and BaOH 870 mμ (7) ; acetylene flame.

Mg, Ca, Sr, Ba (Figs. 3 and 4). The shape of the curve for the resonance line of Mg in an acetylene flame is similar to the shape of the curves for Cu and Ag, and is also characterized by three branches, in which the slope of the line is equal successively to 1, 0.33, and 0.5. In the case of Ca and Sr lines, the curves are characterized by two branches, with slopes of 1 and 0.5, and finally, in the case of Ba, the curve for almost the whole range has a slope of 1. When an illuminating gas flame was used (Fig. 4) the curves had almost the same shape; however, at high concentrations (1.0-0.1 M) the slope of the line became less than 0.5. We shall consider the explanation of this phenomenon below. For the molecular bands of Mg, Ca, Sr, and Ba, both in an acetylene and in an illuminating gas flame, a direct proportionality was observed between the radiation intensity and concentration (the slope of the curve was close to unity) throughout the whole concentration range, apart from the highest (1.0–0.5 M), where the lines bend slightly toward the abscissa.

Y, La, Eu, Yb (Fig. 5). In view of the low radiation intensity of these elements in an illuminating gas flame, measurements were only carried out in an acetylene flame.

The shape of the curve for yttrium is unusual; with its decreasing concentration in solution in the range 1.0 to $5 \cdot 10^{-2}$M the radiation intensity does not decrease but increases. Subsequently the curve becomes a straight line with a slope of 1. The curve for lanthanum is a straight line with a slope of 1 and is slightly curved in the region 1.0 to $2 \cdot 10^{-1}$M. The curves for the LaO bands at 794 and 443 mμ coincide. The curve for europium is also a straight line with a slope approaching unity (1.06). The curve for ytterbium shows a gradually increasing slope.

In Table 2 are given the values of the slope of separate sections of curve, calculated by means of the formula

$$\operatorname{tg} \alpha = \Delta \lg I / \Delta \lg C = (\lg I_n - \lg I_m)/(\lg C_n - \lg C_m).$$

where $\Delta \log \dot{I}$ is the difference between adjacent values of $\log \dot{I}$, while $\Delta \log C$ is the difference between the corresponding values of the logarithm of the concentration of the solution.

Thus, within a concentration range covering two orders of magnitude, the slope of the curve relating $\log \dot{I}$ and $\log C$ changes from values less than unity (0.815) to 1.94.

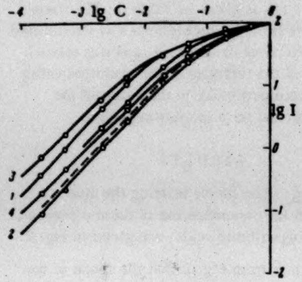

Fig. 4. Relation between log I and log C for Ca 422.7 mμ (1), CaOH 622 mμ (2), Sr 460.7 mμ (3), SrOH 680 mμ (4), Ba 553.5 mμ (5), and BaOH 870 mμ (6); illuminating gas flame.

Ga, In, Tl (Fig. 6). Throughout the whole concentration ranges studied, the curves are straight lines with a slope approximating unity; only in the case of the Tl 377.5 mμ line do we observe strong self-absorption which causes this line to acquire a slope of 0.5 starting at concentrations of $5 \cdot 10^{-3}$ to 10^{-2} M.

Cr, Mn, Fe, Co, Ni (Fig. 7). The curves relating I and C for the lines of these elements, when plotted on a logarithmic scale, consist of two branches: one with a slope of 1 in the initial range, and one with a slope of 0.5 in the region of higher concentrations. However, in solutions with a concentration of 0.5-1 M, the slope of the lines for Cr and Mn is less than 0.5. This may be explained by a delay in evaporation, and to some extent a delay in atomization.

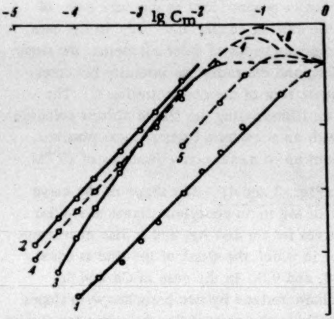

Fig. 5. The relation between log I and log C for LaO 794 mμ (1), Eu 459.4 mμ (2), Yb 398.8 mμ (3), YO 615 mμ (4), YO 615 mμ, inner cone of the flame (5); and also 2.5 cm above the inner cone (6).

DISCUSSION OF RESULTS

The theoretical and experimental curves agree satisfactorily in the majority of cases (see Fig. 1). The three-step shape of the curves for Cu, Ag, and Mg corresponds, according to the curves in Fig. 1, to values of the absorption parameter < 1.0*. The curves for the elements Ca, Sr, Ba, La, Eu, Ga, In, Tl, and Cr, Mn, Fe, Co, Ni (acetylene flame) consist either of one branch with $\tan \alpha = 1$, or, in some instances also, of a second branch with $\tan \alpha = 0.5$ in the high-concentration region. Thus, they too correspond to what is theoretically expected. The exceptions are the curves for Ca, Sr, and Ba (illuminating gas flame, see Fig. 4) and for Y and Yb (see Fig. 5). In the first case, in the concentration range 1.0—0.1—0.2 M, after the branch with $\tan \alpha = 0.5$, there are sections with $\tan \alpha < 5$. Comparison with the curves in Fig. 3 shows that in this case possible decreases in the rate of atomization on going over to more concentrated solutions cannot play a part, since such a phenomenon would also be observed in an acetylene flame. In the second case, the curve for ytterbium in the low-concentration region has a slope which increases to $\tan \alpha = 2$, while in the case of yttrium, as the concentration increases above $5 \cdot 10^{-2}$M, the radiation intensity does not increase but decreases.

The Reasons for the Distortion of the Shapes of the Curves in the Case of Concentrated Solutions of Ca, Sr, and Y Salts. The first possible reason would appear to be difficulties in atomization on increasing the concentration of the solutions or an increase in evaporation with the formation of large coarse aerosol particles in the latter instance. In order to establish to what degree this factor is operative, experiments were carried out in which

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* In [4], using another method, the value of the parameter a established for the Cu 327.4 mμ line was 0.46, for Ag 328.1 mμ 1.03, and for Ag 338.3 mμ 0.96. In addition to these, the values of a < 1 for Ca 422.7 mμ (0.46), Cr 225.4 mμ (0.54), and Ni 352.4 mμ (0.54), found in the course of the same work, contradict the shapes of the curves which we obtained.

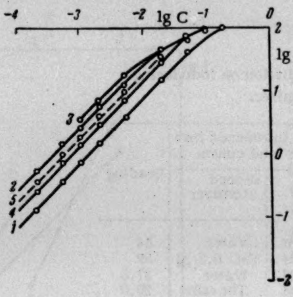

Fig. 6. The relation between log I and log C for Tl 535.0 mμ (1), Tl 377.5 mμ in an acetylene flame (2), Tl 377.5 mμ in an illuminating gas flame (3), Ga 417.2 and 403.3 mμ (4), In 410 mμ and 451 mμ (5).

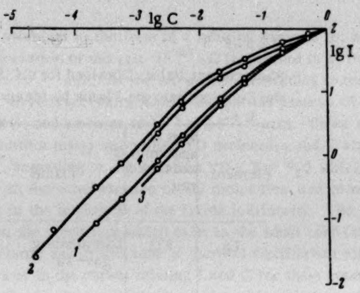

Fig. 7. The relation between log I and log C for Cr 425.4 mμ (1), Mn 403.3 mμ (2), Fe 373.3 mμ, 385.6 mμ, Co 352.5 mμ, 345.4 mμ, and Ni 341.5 mμ (3), Ni 352.5 mμ (4).

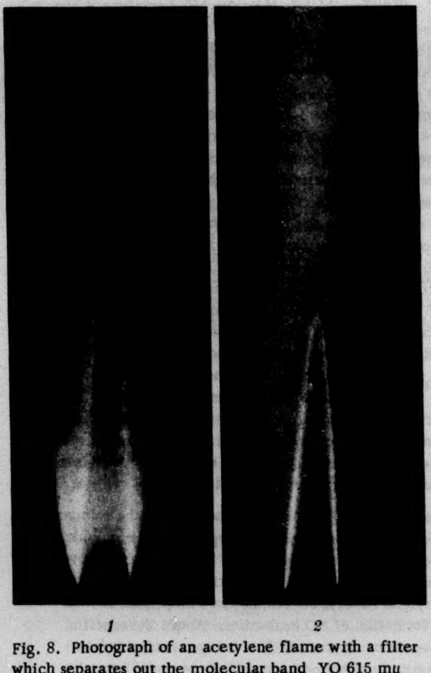

Fig. 8. Photograph of an acetylene flame with a filter which separates out the molecular band YO 615 mμ (SZS-7 and SS-12), on introducing a solution of a Y salt with a concentration of 1M(1) and 0.02 M (2).

two similar atomizers feeding one burner were used. The experimental technique has been described previously [8]. The values of the photocurrents for a more concentrated salt solution (on introducing the solution through one atomizer) were compared with those of more dilute solutions fed through the two atomizers and also through one alone. The results obtained are given in Table 3.

As is evident from Table 3, in the case of Ca and Sr, the reading for the more concentrated solution is somewhat less than that which is obtained on introducing solutions with a total concentration equal to that of the initial concentrated solution through two atomizers; thus, to some extent, one of the reasons for the smaller increase in the photocurrent with increasing concentration is the difficulty involved in atomizing or evaporating the metal from the aerosol particles. In addition, processes which occur in the flame itself play an important role, since the reading of the photocurrent for the two solutions introduced through two atomizers is less than the sum of the readings for each of the solutions taken separately. In the case of yttrium, the photocurrent for either of the solutions decreases on additional introduction of yttrium into the flame through another atomizer; this also testifies to the fact that the decrease in the intensity of the molecular band of yttrium in the flame with increasing yttrium concentration is caused by processes which occur in a flame containing radiating molecules, and not by a change in the character of the atomizing of the solution, or by changes in the way in which yttrium passes into the flame during evaporation of the aerosol particles.

TABLE 3

Photocurrent Values Obtained for Ca, Sr, and Y Radiation on Introducing the Solutions into the Flame by Means of Two Atomizers

Element	Part of spectrum measured, mμ	Flame	Solution introduced into flame and concn.		Reading
			first atomizer	second atomizer	
Ca	622	Illuminating gas—air	Ca 0,5 *M*	Water	54
			Ca 0,3 *M*	CaO 0,2 *M*	59
			Ca 0,3 *M*	Water	37,5
			Ca 0,2 *M*	The same	29,0
Ca	622	The same	Ca 0,2 *M*	"	29,0
			Ca 0,1 *M*	CaO 0,1 *M*	31,5
			Ca 0,1 *M*	Water	17,3
Sr	680	" "	Sr 1,0 *M*	Water	100
			Sr 0,5 *M*	Sr 0,5 *M*	105,5
			Sr 0,5 *M*	Water	68
Sr	680	" "	Sr 0,5 *M*	Water	68
			Sr 0,3 *M*	Sr 0,2 *M*	75
			Sr 0,3 *M*	Water	53
			Sr 0,2 *M*	-	42
Y	615	Acetylene — air	Y 0,1 *M*	Water	145
			Water	Y 0,2 *M*	123
			Y 0,1 *M*	Y 0,2 *M*	95
Y	615	" "	Y 0,2 *M*	Water	140
			Water	Y 0,5 *M*	77
			Y 0,2 *M*	Y 0,5 *M*	61

Another possible reason for the distortion is the shape of the I vs C curves— the processes of light absorption and rotation of lines— is also improbable since on introducing concentrated salt solutions into the flame there is a sharp change in the nature of the radiation in various zones of the flame. Thus, a bright luminosity of the zone near the inner cone of the flame is observed [9], while the luminosity zone of the flame gases above the inner cone obviously weakens. This phenomenon is particular clearly manifested when yttrium is introduced into the flame, as can be seen in Fig. 8. The distribution of brightness in the various zones of the flame on introducing concentrated and dilute solutions of yttrium salts (Fig.9) is characteristic; while in the latter instance the greatest brightness is observed in the central zone of the flame above the inner cone (Fig. 9, 1), in the first instance the brightest part is that at the base of the inner cone of the flame (Fig. 9, 2). In order to obtain these curves the flame was focused by means of a condenser on a spectroscope slit 2 mm in height; the burner was then moved vertically. These phenomena can be explained as follows.

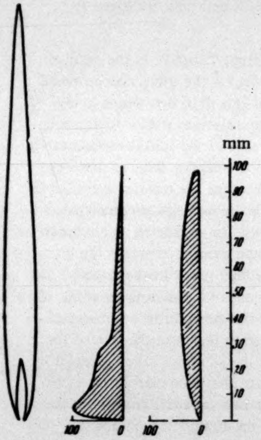

Fig. 9. Distribution of brightness of the luminosity of YO along the height of the flame, on introducing into the flame a 1 M solution of a Y salt (1) and a 0.02 M solution of a Y salt (2); the maximum radiation obtained on using a 1 M solution of a Y salt was taken as 100% brightness.

In the inner cone of the flame, in the zone of the primary burning reaction, the concentration of oxygen atoms is considerably higher than the equilibrium concentration [10] (according to the results given in [11] it is about 760-1500 times higher in the case of an air—acetylene flame); accordingly, we have here favorable conditions for formation of YO molecules. Above the reaction zone, in the part of the flame which is being measured photometrically the oxygen atom concentration is less, and here the yttrium atoms will be in excess with respect to the oxygen atoms. Actually, as we have pointed out earlier [8], the total partial pressure (in atmospheres) of the metal atoms introduced into the flame by the atomizer in the form of a solution amounts to, assuming complete dissociation of the salt, $10^{-3.7}\cdot C$ (expressed in M), or , for a 1 M solution $10^{-3.7}$ atm. At the same time, according to results given in [12], in rich acetylene flames the partial pressure of oxygen atoms p_O is less, and amounts to 10^{-4} to $10^{-4.12}$ atm. Under these conditions a further reaction between YO molecules and Y atoms is possible, e.g., according to the equation $YO + Y \rightarrow Y_2O$, which leads to a decrease in the concentration of YO molecules, and consequently, to a decrease in the brightness of the flame luminosity. The differences between the conditions which exist in the inner cone (reaction zone) of the flame and in the zone of thermal equilibrium also show up in differences in the curves relating I and C for these zones (Fig. 5, Curves 5 and 6); for the curve obtained on making photometric measurements of the reaction zone, the phenomenon of the decrease in radiation intensity with increasing concentration is manifested to a considerable lesser extent. Similar explanations are also valid for the case of Ca and Sr.

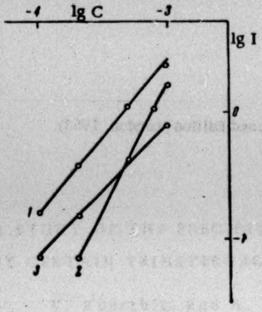

Fig. 10. Curve relating log I and log C for Yb 398.8 mμ (1), Yb + 0.01 M Cs (2), Yb + 0.01 M Ce (3) .

Obtaining the Parts of the Curves with tan $\alpha > 1$ for the Case of Ytterbium when the Concentration is less than $5\cdot 10^{-5}$M. As shown in a previous paper [5], a similar phenomenon is observed in the case of the readily ionized alkali metals (K, Rb, Cs), and is explained by ionization which leads to the "disappearance" of a part of the neutral atoms and their replacement by ions. This explanation cannot, however, be applied to the case of ytterbium, because of its high ionization potential (−6.25 ev), and also because the slope of the curve does not become equal to 1, on addition to the Yb solution of a salt of a readily ionizable metal (cesium) which can suppress ionization of Yb (Fig. 10). In addition, the curve relating log I and log C for ytterbium assumes a slope equal to unity in the presence of an excess of another rare earth element which can combine with the oxygen atoms (cerium, see Fig.10). A possible reason for the fact that curves with tan $\alpha > 1$ are obtained in the case of Yb is therefore the formation, at low concentrations of the metal atoms, of other compounds apart from the YbO molecules which are normally present in the flame compounds which probably contain a larger number of oxygen atoms (of the type MeO_2). This also lead to the disappearance of part of the atoms and to the fact that curves with tan $\alpha > 1$ are obtained.

Alekseeva and Mandel'shtam [13] were the first to point out the significance of the various conditions in the inner and outer cones of the flame for the excitation processes of metals. The observations made in the present article confirm these results, and moreover, indicate the possibility of the stepwise formation in the flame of various compounds between the elements and oxygen, compounds which have properties in common with oxygen. We should note that Y, like some other elements (B, La, Si), has the highest dissociation energy of the oxides, more than 160 kcal/mole [14].

SUMMARY

Curves has been obtained relating the radiation intensityand concentration of 18 elements , when the latter are determined by the flame-photometric method. The deviation from the theoretical shape, which is observed in the case of Ca and Sr (illuminating gas flame) and Y and Yb (acetylene flame), can be explained on the basis of a stepwise formation of oxide molecules of varying composition in the flame.

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A STUDY OF THE PRECIPITATION OF THE ALKALI METALS BY CERTAIN TRIHETEROACIDS

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Heteropolyacids form sparingly soluble compounds with the cations of the alkali metals; the solubility of these compounds decreases as the atomic number of the metal increases. Their solubility also depends to a considerable extent on the nature and the concentration of the mineral acid in the test solution. This makes it possible to select conditions such that differences in the solubility of the salts formed between the heteropolyacids and the various alkali metals will become evident. Accordingly, diheteroacids have already been in use for some time in analytical chemistry [1] for the separation and determination of the alkali metals. For example, silicotungstic acid has been used for separating rubidium and cesium [2, 3]. Silicomolybdic acid has been used for separating rubidium and potassium [4, 5], while potassium has been determined gravimetrically be means of phosphomolybdic acid [6].

Heteropolyacids have also been used in recent years in radiochemistry. Phosphotungstic acid is a selective coprecipitant for radioactive cesium [7], and permits separation of cesium from the other long-life fission products (of uranium) produced by slow neutrons. Coprecipitation of the radioisotopes of cesium and francium with free silicotungstic or phosphotungstic acids in concentrated hydrochloric acid has been used for separating these elements from other products obtained by the bombardment of thorium by high-energy protons [8, 9].

The aim of the work described here was to study the precipitation of the alkali metals with triheteroacids, which have hitherto only been used for the photometric determination of the elements which enter into their composition, e.g., phosphorus, vanadium, and molybdenum, in various materials [10-12].

The problem of separating the alkali elements has still not been completely solved; accordingly the search for new precipitants for these elements is of great practical importance.

Triheteroacids can give sparingly soluble salts with the alkali elements. It is to be expected as well that there should be large differences in the solubility of the salts of the individual metals.

Silicotungstovanadic, phosphotungstovanadic, and phosphomolybdenotungstic acids, which have been studied in detail by Kokorin [13], were chosen for study. A study was made of the relation between the extent of precipitation of potassium, rubidium, and cesium by these acids as a function of the concentration of hydrochloric and nitric acids. The extent of precipitation was determined with the help of the radioactive isotopes K^{42}, Cs^{134}, and Rb^{86}, the radioactive purity of which was controlled by measuring the half-life period and the energy of their β-radiation. A study was also made of the coprecipitation of ultrasmall amounts of rubidium and cesium with the free acids, and attempts were made to establish conditions for separating rubidium from cesium for various ratios of these elements to each other.

Precipitation of the Alkali Elements by Triheteroacids from Hydrochloric and Nitric Acid Solutions. The extent of the precipitation of potassium, rubidium, and cesium was studied by means of the following triheteroacids*: $H_8[Si(W_2O_7)_5V_2O_6]nH_2O$, $H_7[P(W_2O_7)_5V_2O_6]nH_2O$, and $H_7[P(Mo_2O_7)_5V_2O_6]nH_2O$.

The experimental procedure consisted of the following. Into centrifuge tubes with a capacity of 0.8 ml, the internal surface of which had been covered with a hydrophobic film of chlorosilane, was introduced a solution of the chloride or the nitrate of the alkali metal containing $1.04 \cdot 10^{-5}$ g-atom of metal, and a solution of an appropriate indicator. The amount of the salt of the alkali metals in the indicator solutions was $2 \cdot 10^{-6}$ g/ml in the case of cesium and rubidium, and 5 mg/ml for potassium. A solution of the triheteroacid containing $1.17 \cdot 10^{-5}$ g/ml was then added, followed by a hydrochloric or nitric acid solution in an amount such that the total volume of the final mixture was 0.37 ml; the concentration of the acids was varied in separate experiments from 0.5 to 8.5 M. The appropriate acid solutions were prepared by diluting fuming nitric acid (21 M), obtained by distillation, and fuming hydrochloric acid (14 M), obtained by passing gaseous HCl through concentrated hydrochloric acid cooled with solid carbon dioxide. The mixtures were heated for five minutes on a water bath at a temperature of about 50°. The mixture was then cooled with stirring to 1°; the precipitate was centrifuged and washed. Usually, the activity of an aliquot of the filtrate (0.01 ml) was measured after evaporating it on glass targets. Measurements were made with a standard TM-20 end counter, using a type BK-2 setup at a distance of 15 mm from the counter window. The value of the activity varied from 40 to 5000 cpm. The measurement time was varied so that the statistical counting error did not exceed 5%. When the activity of the filtrate was high, differing only insignificantly from that introduced, the activity of the precipitate dissolved in 0.1 M NaOH was also measured.

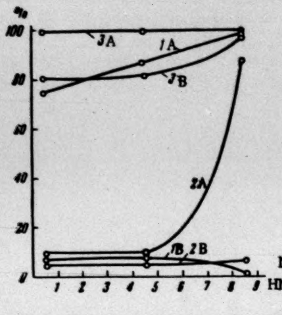

Fig. 1. The relation between the extent of precipitation of rubidium (1b, 2b, 3b) and cesium (1a, 2a, 3a) with triheteroacids, as a function of nitric acid concentration.

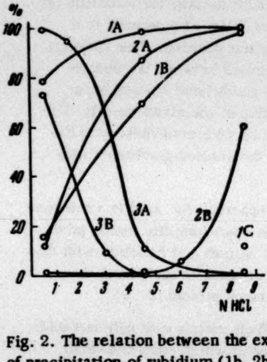

Fig. 2. The relation between the extent of precipitation of rubidium (1b, 2b, 3b) and cesium (1a, 2a, 3a) with triheteroacids, as a function of hydrochloric acid concentration.

Preliminary experiments showed that in the case of sparingly soluble precipitates, no further increase in the completeness of precipitation was observed even on standing for 24 hr. In order to separate comparatively readily soluble salts, a fairly long time (about 12 hours) was necessary. In these cases the precipitates were filtered off at the end of this period.

The results of the experiments carried out in this way (Fig. 1 and 2) permit the following conclusions to be drawn.

1. In nitric acid solutions, complete precipitation of cesium with phosphomolybdenotungstic acid (Curve 3a, Fig. 1) and almost complete precipitation of cesium with phosphotungstovanadic acid, and of rubidium with phosphomolybdenovanadic acid (Curves 1a and 3b respectively) is observed. Moreover, the completeness of the separation of these precipitates does not change at all for the first precipitate, or only changes very insignificantly for the last two precipitates, in the nitric acid concentration range 0.5–8.5 M. For the salts of rubidium with phosphotungstovanadic and silicotungstovanadic acids (Curves 1b and 2b), a characteristic feature is the high solubility which changes little within the given nitric acid concentration range. These salts are hardly precipitated at all. A very small amount (about 10%) of the salt of cesium with silicotungstovanadic acid (Curve 2a) is precipitated at a nitric acid concentration of 0.5 to 4.5 M; on increasing the acid concentration further, the solubility of this salt decreases strongly, and in 8.5 M solutions it is precipitated to the extent of more than 80%.

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* For convenience we shall use the following abbreviations: HSiWV, HPWV, and HPMoV.

2. The picture is slightly different in hydrochloric acid solutions. The dependence of the extent of the precipitation of the compounds studied on the hydrochloric acid concentration (Fig. 2) is more cleary marked. The extent to which the salts of phosphomolybdenovanadic acid (Curves 3a and 3b) are precipitated decreases strongly as the acid concentration increases from 0.5 to 4.5 M; for cesium silicotungstovanadate (Curve 2a) and rubidium phosphotungstovanadate (Curve 1a), on the other hand, a characteristic feature is the very considerable increase in completeness of precipitation of these salts with increasing hydrochloric acid concentration. Rubidium silicotungstovanadate is hardly precipitated at all in solutions where the hydrochloric acid concentration is less than 4.5 M; subsequently the extent of precipitation starts to increase, and at a concentration of 8.5M, it amounts to 60%. It is only in the case of the precipitate formed between cesium and phosphotungstovanadic acid (Curve 2a) that a not very significant change is observed in the extent of the precipitation with changes in the hydrochloric acid concentration.

TABLE 1

Element	Acid	HNO_3 concentration, M 0,5	4,5	8,5
Cs	HPWV	75,8	86,2	98,3
	HPW	99,9	99,9	99,9
Rb	HPWV	7,5	7,6	1,0
	HPW	99,7	99,9	99,8
K	HPWV	Not precipitated		
	HPW	95,6	98,2	99,0

TABLE 2

Molar ratio	Extent of precipitation				Value of the molar ratio
	Cs		Rb		
Cs:Rb:HPWV	%	M	%	M	Rb/Cs
1:1 :1,12	99,0	0,99	67,7	0,68	0,68
1:5 :1,12	91,2	0,91	57,5	2,85	3,15
1:25:1,12	51,1	0,51	15,4	3,85	7,52
1:2 :0,31	56,0	0,56	5,1	0,1	0,18
1:22:0,15	36,2	0,36	1,1	0,24	0,67

3. Of all the salts of potassium with triheteroacids studied, only potassium phosphotungstovanadate is precipitated to a slight extent (about 10%) in 8.5 M hydrochloric acid.

The differences which are observed in the extent of precipitation of alkali element salts with triheteroacids can be determined by a number of factors. Of these, probably the most important are the salting-out effects at high mineral acid concentrations, and the decrease in the capacity of the hydrogen cations of the triheteroacids to exchange with the metal cations, leading consequently to a change in the composition of the salts formed with increasing hydrogen ion concentration of the solutions. In addition, in strongly acid solutions, the decomposition of part of the tritheroacids is not excluded, although it is possible that their oxidizing capacities may be manifested in hydrochloric acid solutions. The acid with the highest oxidizing capacity is known to be phosphomolybdenovanadic acid [1]. Almost complete absence of precipitation of its salts at hydrochloric acid concentrations greater than 6M has been observed.

It follows from these results that large differences in the extent of precipitation of rubidium and cesium salts are observed in several instances. This is true above all for their precipitation with phosphotungstovanadic acid from 8.5 M nitric acid solutions. In this case the difference is a maximum and the ratio of the amounts of cesium to rubidium which are precipitated under these conditions is 98.3. The difference is less marked when rubidium and cesium are precipitated with silicotungstovanadic acid from 4.5 M solutions of nitric and hydrochloric acids, and with phosphotungstovanadic acid from a 0.5M nitric acid solution. The fact that these differences in the degree of precipitation of the corresponding salts of rubidium and cesium do exist leads one to question using such differences for separating these elements.

In order to establish the part played by vanadium in the triheteroacid anion on the solubility of their compounds with the alkali elements, experiments were carried out on the precipitation of potassium, rubidium, and cesium with phosphotungstic acid (HPW) from nitric acid solutions. The technique used was similar to that described above.

It is clear from the results given in Table 1 that the presence of vanadium in the heteropolyacid anion favors an increase in the solubility of the salts of the heteropolyacid with the alkali metals. The influence of vanadium is particularly marked in the case of rubidium and potassium. This influence increases with increasing acidity of the solution. For cesium, on the other hand, the solubility decreases with increasing nitric acid con-

TABLE 3

Acid	Element	Degree of precipitation, %		
		HSiWV	HPWV	HPMoV
HNO_3	Cs	32,6	94,8	99,2
	Rb	10,0	14,1	92,6
HCl	Cs	25,5	42,6	86,5
	Rb	13,0	38,4	82,0

centration, and at 8.5 M, the extent to which cesium is precipitated by phosphotungstovanadic and phosphotungstic acid is almost the the same . This influence of vanadium also leads to a large difference in the solubility of the salts of rubidium and cesium with phosphotungstovanadic acid in 8.5 M nitric acid solution.

Separation of Cesium and Rubidium by means of Phosphotungstovanadic Acid. On the basis of the results of the experiments described in the previous section, one might expect that it should be possible to separate rubidium and cesium effectively by means of phosphotungstovanadic acid in 8.5 M nitric acid. However, results of experiments on the separation of rubidium and cesium in various proportions to each other (Table 2) indicate that considerable coprecipitation of rubidium with cesium salts occurs.

The reason for this coprecipitation is, apparently, the isomorphism of the rubidium and cesium salts; this phenomenon is very widespread among heteropolyacid salts [13]. The mixed salts of rubidium and cesium may possess a different solubility under the given conditions.

The extent of the coprecipitation, which may be characterized by the molar ratio Rb/Cs in the precipitate, increases when the heteropolyacid concentration is kept constant. Thus, on increasing the amount of rubidium 25 times the coprecipitation increases 11 times, although under these conditions the amount of rubidium in the precipitate decreases 4.4 times.

A decrease in the coprecipitation of rubidium is observed only on decreasing the amount of phosphotungstovanadic acid in solution. The best results in this connection are obtained for a molar concentration of heteropolyacid in solution which is a tenth of the sum of the molar concentrations of rubidium and cesium. Despite the fact that the rubidium concentration is twice that of cesium, the amount of the former coprecipitated is only 5.1%, while the ratio of the molar concentrations Rb/Cs in the precipitate is equal to 0.18.

A Study of the Coprecipitation of Small Amounts of Rubidium and Cesium with Free Triheteroacids. It has been established [8] that radioactive cesium is coprecipitated from strong hydrochloric acid solutions with free silicotungstic and phosphotungstic acid, while rubidium remains in solution. The resolution factor for cesium and rubidium amounts to 300 under these conditions. In this connection it was interesting to study the behavior of small amounts of these elements during precipitation of free triheteroacids.

Into test tubes treated in the way described above was introduced 20 mg of silicotungstovanadic or phosphotungstovanadic acid (when phosphomolybdenovanadic acid was used the amount taken was 15 mg), 0.1 ml of an aqueous solution of the indicator, and 21 M nitric acid or 14 M hydrochloric acid in such an amount that the final concentration of the solution was 16 M with respect to nitric acid and 12.9 M with respect to hydrochloric acid . The method used was similar in all other respects to that described in the first section.

The experimental results (Table 3) show that ultrasmall amounts of cesium and rubidium (about $2 \cdot 10^{-7}$ g) are precipitated with the free triheteroacids. The extent to which they are coprecipitated is particularly large in the case of the phosphomolybdenovanadic acid precipitate, and is almost independent of the mineral acid used. Almost complete coprecipitation is also observed with phosphotungstovanadic acid from a nitric acid solution. Under such conditions coprecipitation of rubidium is considerably less (6.8 times less). Further experiments showed that reprecipitation of the precipitate of this acid depresses the extent to which rubidium is coprecipitated 2-3 times. Accordingly, this method can be recommended for separating cesium and rubidium. when dealing with very low concentrations of these elements; the recommended method does not take more than 40 minutes. The extent to which cesium is coprecipitated during reprecipitation changes insignificantly.

Comparison of the results on the coprecipitation of rubidium and cesium with free silicotungstovanadic and phosphotungstovanadic acids allows one to conclude that replacement of phosphorus by silicon in the triheteroacid acid anion leads to a decrease in the coprecipitation of these elements. A similar effect is observed on replacing molybdenum by tungsten. Consequently, coprecipitation of rubidium and cesium depends on the nature of the atoms in the triheteroacid anion.

The authors wish to thank A. I. Kokorin for a gift of triheteroacids.

SUMMARY

There are considerable differences in the completeness of precipitation of rubidium and cesium with phosphotungstovanadic and silicotungstovanadic acids from 8.5 M nitric acid solutions. Formation of isomorphous mixed salts of rubidium and cesium, however, complicates their separation.

Comparison of the extent of precipitation of potassium, rubidium, and cesium with phosphotungstovanadic and phosphotungstic acids in nitric acid solutions of varying concentrations shows that the presence of vanadium in the anion of the heteropolyacid favors an increase in the solubility of their salts with the alkali metals, particularly potassium and rubidium.

Free triheteroacids in strongly acid solutions coprecipitate small amounts of rubidium and cesium to a considerable extent. The degree of coprecipitation depends on the concentration of the alkali metal in solution and on the composition of the triheteroacid.

It has been found that small amounts of rubidium and cesium can be separated by means of phosphotungstovanadic acid from nitric acid solutions.

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POLAROGRAPHIC DETERMINATION OF CALCIUM IN LEPIDOLITES AND MUSCOVITES

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In the calcium method of establishing the age of micas it is necessary to determine calcium in amounts which vary, as in the case of lepidolites, within the limit 0.001 – 0.2% [1].

The photometric method of determining calcium with murexide, despite its high sensitivity (1-8 μg Ca in 10 ml), possesses low selectivity, as our experiments showed; colored compounds are formed by Fe, Co, Ni, Mn, Cu, Zn, Ba, Mg, Sr, etc. Accordingly, we established the possibility of using a polarographic method of determining calcium by means of sodium ethylenediaminetetraacetate (EDTA-Na).

One of the methods of using complexons in polarography indicated by Přibil [2] is based on the exchange reactions:

$$\mathrm{Me_I K^{2-} + Me_{II}^{2+} \rightleftarrows Me_{II} K^{2-} + Me_I^{2+}}.$$

The equilibrium of the exchange reaction is determined by the following equation:

$$K = \frac{[\mathrm{Me_{II}K^{2-}}]\,[\mathrm{Me_I^{2+}}]}{[\mathrm{Me_I K^{2-}}]\,[\mathrm{Me_{II}^{2+}}]} = \frac{K_I}{K_{II}}$$

(where K_I and K_{II} are the corresponding instability constants of the complexes of both metals). This equation is applicable to rapidly reacting complexes, so-called "equilibrium complexes" [3]. Such reactions have been fairly throughly studied [4]. It is possible to choose conditions such that, using the various rates of reaction of the exchange, there can occur quantitative displacement of the cations from the complexes by another cation, which forms a complex with a higher instability constant than that of the complex with the replaced cation. For example, Přibil and Vicenova [5] have shown that in an ammoniacal medium it is possible to expel zinc ions from zinc complexonate ($pK_{ZnK^{2-}} = 16.1$) by means of calcium ions ($pK_{CaK^{2-}} = 10.6$) according to the equation

$$\mathrm{ZnK^{2-} + Ca^{2+} \rightarrow CaK^{2-} + Zn^{2+}}$$

and the liberated zinc ions determined polarographically. In this way Přibil et al. have determined calcium in solution [2,5] and in blood serum [6]. We have tried to use the method indicated for determining calcium in lepidolites and muscovites after removal of the main accompanying elements on KU-2 ion-exchange resin.*

EXPERIMENTAL

Measurements were carried out on a V 301 recording polarograph of the Heyrovsky type. The capillary characteristics were as follows: m = 2.715 mg/sec; t = 3.65 sec; $m^{2/3} \cdot t^{1/6} = 2.415\ \mathrm{mg}^{2/3}\ \mathrm{sec}^{-1/2}$. The zinc ethylenediaminetetraacetate solution (EDTA-Zn) was prepared by dissolving (EDTA-Na) and 1.917 g of $ZnSO_4 \cdot 7H_2O$ in a small volume of twice-distilled water, after which 572 ml of concentrated ammonia (prepared by saturating twice-distilled water with ammonia from a cylinder) was added and the volume made up to one liter. The concentration of the solution was $6.6 \cdot 10^{-3}$ M with respect to EDTA-Zn and 8 M with respect to ammonia.

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* See V. I. Baranov and Ch'en Yu-wei, Zhur. Anal. Khim. 15, 163 (1960) [See C.B. translation, p. 183].

Solutions of calcium, barium, manganese, magnesium, strontium and other chlorides were prepared from the chemically pure salts after recrystallization of the latter; a 70% solution of diammonium hydrogen phosphate was prepared by dissolving the chamically pure salt (Merck). A 0.5% gelatin solution was used.

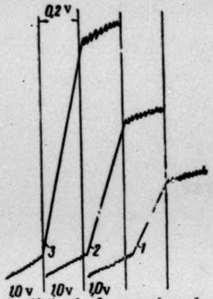

Fig. 1. 1) 1 ml of supporting electrolyte, 0.5 ml of conc. NH_4OH, and 7 drops of 0.5% gelatin; volume made up to 3 ml; 2) after addition of 28 μg Ca; 3) after a second addition of 28 μg Ca (56 μg of Ca in all).

In Fig. 1 are shown polarograms for the supporting electrolyte and for zinc liberated by calcium from EDTA-Zn in ammonia solution.

In order to establish the extent of the liberation of zinc from EDTA-Zn by calcium, as a functionof the ammonia concentration, polarograms were taken for solutions whose concentrations of EDTA-Zn and calcium chloride were constant, but whose ammonia concentrations varied.

Experiments showed that within the range 4-9.6 M ammonia quantitative replacement of zinc from EDTA-Zn by calcium ions occurs.

In Fig. 2 are shown results which demonstrate the effect of EDTA-Zn concentration on calcium determination. As Fig. 2 shows, the difference in the currents between curves 2 and 1 decreases at high and low concentrations of EDTA-Zn. The optimum EDTA-Zn concentration lies within the limits $1.2 \cdot 10^{-3}$–$2.2 \cdot 10^{-3}$M . In order to establish the possibility of carrying out a quantitative determination of calcium in lepidolites and muscovites, from 1 to 8 μg calcium/ml was added to a solution of EDTA-Zn. The relation between the diffusion current for zinc and the calcium concentration is shown in Fig. 3.

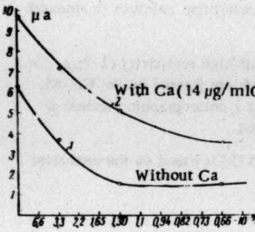

Fig. 2.

It is known that during the polarographic determination of calcium on the basis of the zinc wave, interference from magnesium can be eliminated by adding ammonium phosphate to the solution. There is no published information regarding the effect of manganese* on the determination of calcium by this method. Accordingly, experiments were carried out on the determination of calcium in which manganese was masked with ammonium phosphate (in the same way as magnesium is masked). For this purpose to several test tubes, each containing 1 ml of $6.6 \cdot 10^{-3}$M EDTA-Zn, was added 0.1 ml of a 70% ammonium phosphate solution, an equal volume of calcium chloride, and varying amounts of manganese sulfate; ammonia solution was finally added until its concentration was 4—7 M , and then 7 drops of a 0.5% gelatin solution, and the volume made up to 5 ml with water. The solutions were transferred to the electrolyzer, purged with nitrogen, and polarograms were taken. In parallel, polarograms were taken of solutions containing exactly the same components, but with ammonium phosphate left out. Similar experiments were carried out with magnesium. The results obtained are shown in Fig. 4. As is evident from Curves 1 and 2, manganese and magnesium also liberate zinc from EDTA-Zn, thereby leading to high results for calcium. By binding Mn^{2+} and Mg^{2+} with ammonium phosphate it is possible to eliminate interference on the part of these metals completely ** (Fig. 4, Curves 3 and 4). However, when magnesium is present in amounts five times that of calcium, the precipitate of magnesium phosphate adsorbs small amounts of calcium, and the calcium results are somewhat low (Curve 4). Barium and strontium, when present in amounts

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* Using a spectrographic method, about 0.07% Mn was found in the lepidolites, while about 0.03% Mn was found in the muscovites.

** The ammonium phosphate present in solution lowers the zinc diffusion current slightly.

Determination of Calcium in Micas

Mica	Location from which the samples were taken	Calcium found, %	Mean Ca content, %	Deviation from the mean, %
Muscovite	White Sea	0,022		+3,2
		0,021	0,0213	−1,4
		0,022		+3,2
Lepidolite	Voron'ya Tundra	0,0150	0,0175	−12,6
		0,0200		+16,6
Muscovite	Chupa, Kareliya	0,028	0,027	+3,6
		0,026		−3,5
Muscovite	Ukraine	0,035	0,035	—
		0,035		—

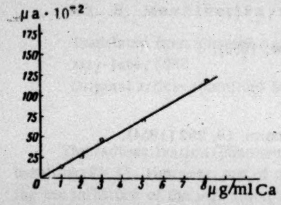

Fig. 3. Relation between the calcium concentration of the solution and the zinc current.

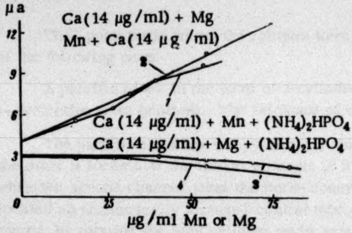

Fig. 4. Effect of manganese and magnesium on calcium determination in the absence and in the presence of ammonium phosphate.

which are twice that of calcium, do not affect the polarographic determination of calcium by the method indicated; when they are present in greater amounts, high results are obtained. When phosphate is present in the solution, barium and strontium do not affect calcium determination.

We also tried EDTA-Co*, $pK_{CoK^{2-}} = 16.1$, instead of EDTA-Zn and found that calcium liberates cobalt from EDTA-Co in an equivalent amount ($CoK^{2-} + Ca^{2+} \rightarrow CaK^{2-} + Co^{2+}$).

Consequently, the calcium concentration of the solution can also be determined from the wave height for cobalt. Our experiments showed that manganese and barium do not essentially affect the results for calcium determinations based on the cobalt wave. Magnesium and strontium interfere with the determination of calcium based on the cobalt wave. When, however, phosphate is added, interference from strontium can be eliminated but magnesium leads to a deterioration in the shape of the curve and makes it difficult to measure.

On the basis of this work, the following method has been developed for the determinationof calcium in lepidolites and muscovites: 1 g of sample is decomposed with 40 ml of concentrated pyrophosphoric acid, phosphoric and silicic acids are then removed on the cation exchange resin KU-2 (the rate at which the solution is passed through the resin column should be 2 ml/min). The aluminum is first eluted from the column by means of concentrated ammonia until the eluate gives no reaction with alizarin S; calcium and the other cations are then eluted from the column with 3 N HCl at the rate of 2 ml/min. The hydrochloric acid solution is evaporated on the water bath to dryness; the residue is dissolved in water, adding the latter in small portions. The solutions are poured into a test tube with a capacity of 5 ml, and the volume made up to the mark with water. Two ml of the solution is transferred to a 10 ml standard flask, 2.5 ml of $6.6 \cdot 10^{-3}$M EDTA-Zn solution, 1 ml of concentrated ammonia solution, 0.1 ml of 70% diammonium hydrogen phosphate, and 7 drops of a 0.5% gelatin solution are added, and the volume finally made up to 10 ml.

The solution is placed in the electrolyzer and is purged with nitrogen (or hydrogen) for 5-10 minutes, then polarograms are taken. The calcium concentration is determined by comparing it with a standard solution containing the same components as the test solution, or by means of a calibration curve. Several samples of lepidolites and muscovites were analyzed by the method indicated. The results obtained are given in the table.

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* 2.48 g of EDTA-Na and 1.9588 g $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in a small volume of twice-distilled water, 572 ml of concentrated ammonia was added, and the volume made up to one liter with water.

SUMMARY

A method is suggested for the determination of calcium in lepidolites and muscovites; it is based on removing a number of the accompanying elements (P, Si, Al, etc.) on a KU-2 ion exchange resin, and subsequently determining calcium in the eluate by a polarographic method, on the basis of the wave for zinc which is obtained as a result of an exchange reaction between EDTA-Zn and calcium ions.

Interference from manganese, barium, strontium (and magnesium) during the polarographic determination of calcium on the basis of the zinc wave, can be eliminated by adding ammonium phosphate to the solution.

It has been shown that on replacing EDTA-Zn by EDTA-Co, satisfactory results can also be obtained for calcium when the latter is determined on the basis of the cobalt wave. In this case manganese and barium do not essentially affect the determination of calcium; strontium does not interfere with the determination of calcium in the presence of phosphate, while magnesium interferes by spoiling the shape of the curve.

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A RADIOACTIVATION METHOD FOR THE DETERMINATION OF BERYLLIUM IN MINERAL RAW MATERIALS AND IN HYDROMETALLURGICAL PRODUCTS

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The radioactivation (photoneutron) method has been widely used in recent years for the determination of beryllium [1-4]. However, one of the basic difficulties of the radioactivation method—the necessity of eliminating the influence of the self-absorption of the photoneutrons by the material of the sample—has still not been positively overcome. In addition, the setups which have been described are not of a sufficiently advanced design. The present article contains a description of the radioactivation techique used in our laboratory for the determination of beryllium.

APPARATUS

The apparatus in which the samples were irradiated and in which the neutrons were recorded (Fig. 1) consists of the following parts.

A paraffin block in the form of a cylinder 300 mm in height and diameter serves both as a retarder of and as protection from neutrons. The thickness of the protective layer is about 100 mm in all directions.

The paraffin block has two cylindrical channels, one of which is located in the center of the block, while the other is located at the side, at an angle of 27°. The first channel is designed to take the sample and the source while the second channel takes the boron counter. Into the first channel is introduced a lead cylinder in which is located an eccentrically arranged central tube plus source, and a sample holder plus sample which surround the source. By rotating the lead cylinder on its axis, it is possible to bring the sample and the source up to the boron counter or remove them from the latter, and at the same time alter the thickness of the lead layer in the space between the sample and counter (Fig. 2).

Lead in the form of an incomplete cylinder with a thickness of 20 mm is fused into the paraffin block to protect the operator from γ-rays.

The lead screen used as a protection from γ-rays consists of three layers. In order to cut down on the weight, only the front part of the setup is protected by three layers of lead, the over-all thickness at the front being 100-120 mm. Such protection permits the use of a γ-source with activities up to 200 mC.

The sample holder, by means of which the test samples are introduced into the setup, is in the form of a cylinder consisting of three parts. The lower part is filled with lead; the middle section is an empty semicylinder in which the sample is placed during the time measurements are being made; the upper part is filled with granulated lead embedded in paraffin and is sealed with a lead stopper (Fig. 3). When samples are being changed, the sample holder is not withdrawn completely from the setup; its lower end is left in the apparatus so as to afford protection against γ-radiation.

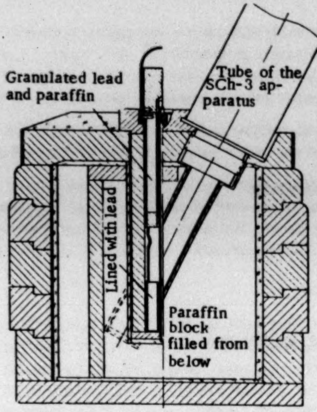
Granulated lead and paraffin
Tube of the SCh-3 apparatus
Lined with lead
Paraffin block filled from below

Fig. 1. Setup for the radioactivation determination of beryllium.

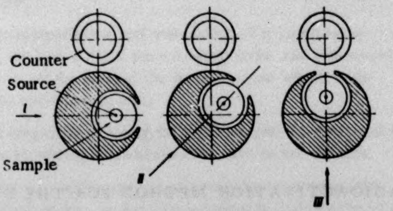

Fig. 2. Three positions of the source and sample with respect to the boron counter.

The source holder is placed in a tube fastened onto a stand. It is a cylinder 6 mm in diameter and 250 mm long, lined with lead along its whole length, with the exception of a small empty section in which the γ-source is placed.

The spaces in which the test samples are placed are in the form of cylinders with double walls 70 mm long. The thickness of the layers of samples is determined by the gap between the walls, and amounts to 5, 10, and 15 mm.

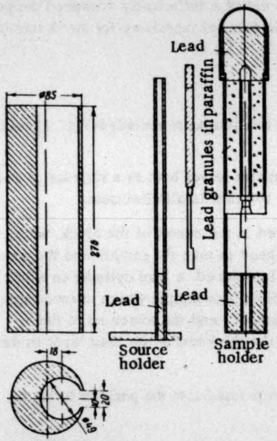

Fig. 3. Cross-sections of the lead cylinder, source holder, and sample holder.

The γ-source is an antimony rod 50 mm long and weighing about 1.5 g, enclosed in an aluminum ampoule. The γ-radiation source is Sb^{124}.

The neutrons were recorded by an industrial SCh-3 apparatus provided with a SNMO-5 counter.

When the operating conditions have been chosen correctly, the background of the apparatus, in the presence of a γ-source giving a field of the order of 10^4 μr /second, does not exceed 1 cpm.

The operating conditions are chosen by determining the characteristics in the presence of the γ-source by means of some beryllium preparation.

From the family of characteristics which are taken by varying the high voltage applied to the counter, and the threshold acutation of the amplitude discriminator, the characteristic is chosen which has a plateau with the least slope (Figs. 4a, b, and c).

Effect of the Self-Absorption of the Photoneutrons and the Absorption of γ-Rays. One of the most fundamental problems in developing a method for the radioactivation determination of beryllium is the problem of eliminating the influence of the self-absorption of the neutrons by elements with a high cross-section of neutron capture which are present in the sample. Self-absorption of neutrons slowed down to thermal energies plays a basic role.

The number of thermal neutrons in the volume occupied by the sample is determined in the main by the number of neutrons diffusing into the sample from the layers of retarder lying adjacent to it. If it is assumed that the thermal neutrons diffuse from the retarder layer, the thickness of which is equal to the diffusion line (2-3 cm), then, according to the law of the distribution of thermal neutrons, the number of such neutrons in the volume oc-

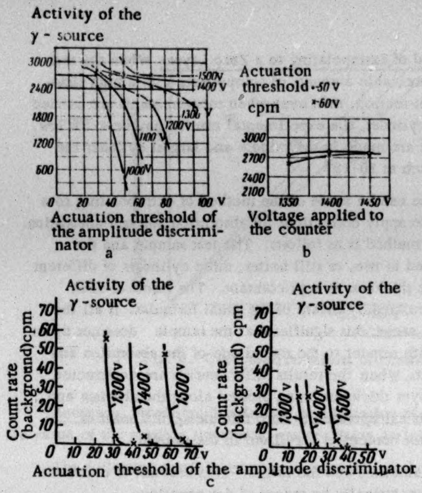

Fig. 4. Counting characteristics of the apparatus. Fig. 4a and 4b were taken with a beryllium preparation; 4c is the characteristic of the apparatus background.

TABLE 1

(2.5 g BeO added)

Base, g	Count rate in the absence of cadmium		Count rate in the presence of cadmium	
	cpm	% (relative)	cpm	% (relative)
Al_2O_3	1450	100*	1270	88
CaF_2	1400	97	1250	86
H_3BO_3	1250	86	1180	81
$Na_3BO_3 \cdot 10H_2O$	1220	84	1150	79
Li_2CO_3	1360	94	1270	88

* The count rate for a mixture of Al_2O_3 + BeO was taken as 100%.

cupied by the sample amounts to, under our conditions, 10-20% of the total number of thermal neutrons. Accordingly, the maximum value of the self-absorption of neutrons is also approximately evaluated by the same magnitude. Therefore, the relation between the magnitude of self-absorption and the amount of detrimental components in the sample is expressed by a saturation function [5]. The saturation phenomenon reduces to the fact that there exists some limit above which the self-absorption effect does not increase in the case of even very considerable concentrations of detrimental components. The value of this limit depends, in the main, on the geometry of the sample. When the volume of the sample is limited by the dimensions of the cylinders given above, the maximum error arising as the result of self-absorption amounts to 15-20% (relative).

In Table 1 are given the results of measurements of synthetic mixtures made from chemically pure reagents and beryllium oxide. The amount of the latter, and also the volumes of the mixtures were the same. One of the series of measurements was carried out under the usual conditions, while in the other series of measurements, the cylinder with the sample was enclosed in a cadmium sheath (with a wall thickness of 1 mm) which absorbs the thermal neutrons passing in and out of the sample.

From the results given in Table 2 it follows that the maximum difference in the count rate for individual mixtures amounts to 16% when no cadmium screen is used, and to 10% when such a screen is used. As one might expect, mixtures with a high content of boron and lithium had the highest self-absorption. It should be pointed out that the cadmium filter brings together, but does not level out the count rate completely. This indicates that a significant part is played in self-absorption by the self-absorption of epithermal neutrons.

When the sample and the standard differ in bulk density, errors may arise because of unequal absorption of the γ-rays by sample and standard. Calculations have shown that when the thickness of the layer of sample and standard does not exceed 10-15 mm, the maximum error which can arise because of unequal density does not exceed 2-3%.

Methods for Eliminating or Lowering the Effect of the Self-Absorption of the Neutrons and the Absorption of γ-Rays.

a) Correct Choice of Sample Size. When the sample and standard are measured in the smallest of the cylinders listed above, errors arising from absorption and self-absorption are almost completely eliminated in most cases.

In the larger cylinder it is possible to analyze samples with low beryllium content (< 0.01%), and also samples which do not give rise to doubts as to the identity of their chemical composition with the chemical composition of the standard.

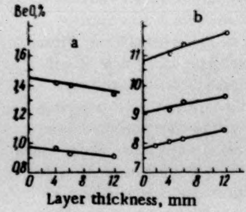

Fig. 5a and 5b. The method of obtaining the correct result by extrapolating to zero thickness of the layer.

b) The Method of Extrapolating to a Zero Layer. When the test samples contain appreciable amounts of components with a high slow-neutron capture cross-section, then even when measurements are carried out in the smallest cylinder, the experimental results may be 4-5% low. When measurements are made in the middle and largest cylinder the errors may be as much as 10-15%.

In this case, use can be made of the method of extrapolating to a zero layer in order to apply corrections for absorption and self-absorption. The essence of this method is as follows. The test sample and the standard are measured in two, or still better, three cylinders of different size, while the layer thickness is kept constant. The result of each measurement is calculated by means of the usual formulas. If all the results should be the same, this signifies that the sample does not differ from the standard with respect to the magnitude of the absorption and self-absorption effects. When the results differ, curves are constructed on their basis, the layer thickness being plotted along the abscissa and the result obtained along the ordinate. The curve obtained is extrapolated to zero thickness; the point of intersection of this curve with the ordinate gives the sought for content of beryllium in the sample.

When a sample is analyzed in only two cylinders—the smallest and the largest—it is best not to construct a curve. In this case the required analytical result is found analytically by means of the equation:

$$K_0 = K_1 - (K_2 - K_1)/2, \qquad (1)$$

where K_1 is the result obtained on using the small cylinder, K_2 is the result obtained on using the large cylinder, and K_0 is the true result.

In Fig. 5a is shown a curve constructed on the basis of the analysis of two samples in which absorption and self-absorption were greater than in the standard, while in Fig. 5b is shown a curve constructed on the basis of the results obtained with three samples, in which they were lower than in the standard.

c) The Internal Standard Method. The essence of the internal standard method is the use as a standard of a mixture composed of the test sample and a certain amount of beryllium oxide (high-purity material).

The amount of beryllium oxide in the mixture should not exceed 5% of the weight of the sample being analyzed, while the count rate of the mixture should be approximately twice that of the sample itself.

After careful mixing, both the mixture obtained and the original sample are measured under identical geometrical conditions, the total weight of the mixture used being equal to the weight of original sample.

The results of the measurements are calculated by means of the formula:

$$K_{sa} = K_{st} \frac{P_{st}}{\frac{I_{mi}}{I_{sa}} P_{mi} - P_{sa}}, \qquad (2)$$

where $K_{standard}$ is the beryllium oxide concentration of the standard, $P_{standard}$ is the weight of the added beryllium oxide, P_{sample} is the weight of sample in the mixture, $P_{mixture}$ is the weight of the mixture, I_{sample} is the count rate of the original sample, and $I_{mixture}$ is the count rate of the mixture.

The following is an illustration of the use of the internal standard method:

Weight of original sample 34 g; count rate of the sample 300 cpm; the mixture was made from 33 g of sample and 1 g of beryllium oxide (99.5% BeO); count rate from the mixture 775 cpm.

$$K_{sa} = 99{,}5 \frac{1}{\frac{775}{300} \cdot 34 - 33}. \qquad K_{sa} = 1{,}82\%.$$

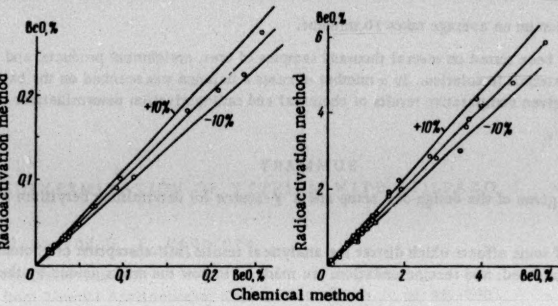

Fig. 6. Comparative results of chemical and radioactivation analyses.

Accuracy, Precision, Sensitivity, and Duration of an Analysis. The accuracy of the results is determined by the value of the possible systematic errors arising during the analytical procedure.

The following possible errors may arise during the radioactivation determination of beryllium:

a) errors in analyzing the standard (2-3%); b) errors caused by self-absorption of neutrons and absorption of γ-rays (1-2% when the measures indicated above are adopted); c) errors caused by inaccurate observation of the geometrical conditions (about 1%). Under unfavorable conditions the total error may be 5-6%.

The precision of the results of a radioactivation determination of beryllium is determined, in the main, by the value of the statistical error with which the measurements are made:

$$\delta(\%) = \frac{100}{I_{sa}}\sqrt{\frac{I_{sa}+I_{ba}}{t_{sa}}+\frac{I_{ba}}{t_{ba}}}, \tag{3}$$

where I_{sample} is the count rate during measurement of the samples; $I_{background}$ is the apparatus background (including the γ-background); t_{sample} is the time it takes to measure the samples; $t_{background}$ is the time it takes to measure the background. When the SCh-3 apparatus is used the background amounts to 1-2 cpm. Accordingly, in most cases, the value of the statistical error is determined by the simplified expression:

$$\delta(\%) \approx \frac{100}{\sqrt{I_{sa}t_{sa}}} \tag{4}$$

The real accuracy of the method (which is characterized by the mean square error of a single determination) amounts to:

for a concentration of the order of thousandths of a percent of BeO 20-30%
for a concentration of the order of hundredths of a percent of BeO 10-20%
for a concentration of the order of tenths or more of BeO 1-10%

If it is assumed that the sensitivity is expressed by the number of impulses per minute I_{min}, which is recorded with a precision of 20%, under conditions where the time taken to measure the sample as well as the background amounts to 25 minutes each, then we get the following relation for I_{min}

$$I_{min} = \frac{1}{2}\left(1+\sqrt{1+8I_{ba}}\right). \tag{5}$$

For a background which is equal to 1 cpm, the minimum count rate recorded by the apparatus is 2 cpm. This corresponds to a sensitivity of a determination of 1mg of beryllium oxide when the activity of the source is 100mC. When samples of the order of 100 g are used the sensitivity of a determination is equal to 0.001-0.002% of beryllium oxide.

One determination on an average takes 10 minutes.

The method has been tested on several thousand samples of ores, enrichment products, and hydrometallurgical products, including materials in solution. In a number of cases a balance was reached on the basis of the analytical results. In Fig. 6 are given comparative results of chemical and radioactivation determinations of beryllium in 60 samples.

SUMMARY

A description is given of the design of a setup and a γ-source for determining beryllium by a radioactivation method.

The influence of some effects which distort the analytical results (self-absorption of photoneutrons, absorption of γ-rays) are considered, and recommendations are made as to how the errors caused by these effects can be eliminated.

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PHOTOMETRIC DETERMINATION OF YTTRIUM WITH STILBAZO

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The reagent stilbazo was suggested for the photometric determination of aluminum by V. I. Kuznetsov [1]. This reagent has subsequently been used for the determination of aluminum in steels [2-5], slags, and copper and lead melts [6]. It has proved suitable for the microdetermination of aluminum [7], for the determination of tungsten [8], indium and gallium [9], and fluorine [10].

Alizarin S [11-14], arsenazo [15], aluminon [16-18] and other reagents which have been suggested for the photometric determination of the rare earths are not selective reagents. The object of the work described in the present article was to study the interaction of yttrium with the reagent stilbazo, with the aim of using it for the selective photometric determination of yttrium.

For these studies a 10^{-3} M solution of stilbazo, prepared from an aliquot of the purified reagent, was used, and a 10^{-2}M solution of yttrium chloride was prepared from the oxalate, the purity of which has been checked spectrographically. The yttrium chloride solution was standardized gravimetrically by the hydroxyquinoline method. Solutions of varying concentration were prepared by dilution of this original 10^{-2}M stock solution.

The absorption curves for the reagent and for the yttrium complex (shown in Fig. 1) were obtained by means of of the UM-2 universal monochromator. They show that in order to measure the optical density of the test solutions, it is necessary to use a green liquid filter prepared from potassium dichromate and cupric sulfate solutions, with a maximum transmission at 540 mμ.

It is best to carry out the reaction between yttrium and stilbazo at a pH of 7.0, since lanthanum does not react at this pH.

Yttrium ions react fairly rapidly with stilbazo. The optical density of solutions of the complex is already constant 10-15 minutes after mixing them. Heating solutions of the complex leads to its decomposition.

A study was made of the effect, on the optical density of the solution of the complex formed, of changing the concentration of one of the reactants while the concentration of the other was kept constant. The results of this study are given in Fig. 2. The effect of stilbazo on the value of the optical density of the solution of the complex was eliminated by subtracting the optical density of the solutions in the corresponding blank tests. Equal excess of stilbazo and of the yttrium salt leads to an unequal change in the optical density of the solution of the complex. This indicates that stilbazo and yttrium do not interact in a molar ratio of 1 : 1.

In order to establish the proportions in which stilbazo reacts with yttrium, the isomolar series method was used [19]. The total concentration of the reacting solutions was $5.4 \cdot 10^{-5}$ and $7.3 \cdot 10^{-5}$M. It follows from Fig. 3 that the maximum deviation of the optical density of the test solutions from the additive values corresponds to a molar ratio of yttrium to stilbazo of 1 : 2. The result obtained for the determination of the composition of the complex by the isomolar series method agrees with the curves shown in Fig. 2.

Solutions of the complex of yttrium with stilbazo follow Beer's law fairly well (Fig. 4).

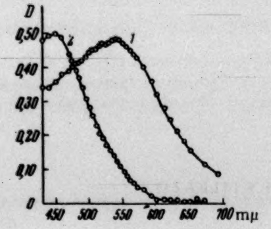

Fig. 1. Absorption curves ot the yttrium complex (1) and stilbazo (2). 1) 0.5 ml of 10^{-3}M stilbazo and 0.5 ml 10^{-3} YCl_3; 2) 0.5 ml 10^{-3}M stilbazo solution. The final volume of the solution was 25 ml in both cases.

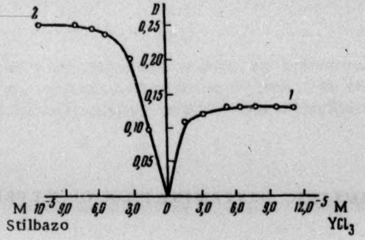

Fig. 2. Relation between the optical density of the solutions and the concentration of yttrium (1) or stilbazo (2) in solution. 1) 1 ml $3.4 \cdot 10^{-4}$M stilbazo solution; 2) 1 ml $3.4 \cdot 10^{-4}$M YCl_3 solution. The final volume was 25 ml in both cases.

Determination of Yttrium with Stilbazo

Yttrium taken, μg	Yttrium found, μg (mean arithmetic)	Mean deviation of a single determination		Probable deviation of a single determination	
		absolute	relative	absolute	relative
12,1	10,9	0,26	2,4	0,20	1,8
18,1	17,9	0,39	2,2	0,38	2,1
24,2	24,9	0,58	2,3	0,58	2,3
30,2	30,7	0,42	1,4	0,37	1,2
In the presence of lanthanum					
18,1	18,6	0,25	1,3	0,22	1,2
24,2	25,3	0,37	1,5	0,26	1,0
30,2	30,2	0,22	0,7	0,22	0,7

The molar extinction coefficient of the complex of yttrium with stilbazo was determined by the saturation method [20]. For this purpose, use was made of the curves given earlier (Fig. 2) relating the optical density of solutions of the complex to excess of one of the reactants. The molar extinction coefficient was found to be about 60,000 when a green filter with maximum transmission at 540 mμ was used. This value indicates the high sensitivity of the reagent tested.

Potassium and sodium do not affect formation of the complex even when they are present in amounts 500 times that of the yttrium; calcium ions do not show any effect when present in amounts 50 times that of yttrium; while magnesium ions do not interfere when present in amounts 30 times that of yttrium. In the presence of lanthanum the optical density of solutions of the yttrium complex increases somewhat, although lanthanum itself at the pH chosen does not interact with stilbazo. Any possible interference on the part of lanthanum was eliminated by adding small amounts of acetone to the test solutions. It is known that the sensitivity of certain reactions may be lowered in the presence of acetone [21]. In our case, addition of acetone to the test solutions probably lowers the sensitivity of the reaction of lanthanum with stilbazo to such an extent that lanthanum does not affect the reaction of yttrium with the reagent. It was established that cerium also does not react with stilbazo at pH 7.0, although elements of the yttrium subgroup—gadolinium erbium—react in the same way as yttrium.

Sodium ethylenediaminetetraacetate, Seignette's salt, pyrophosphate, oxalate, fluoride, ascorbic acid, succinic, azelaic, and adipic acids, also in small amounts lead to a lowering of the color of the yttrium complex. This indicates that the stability of the complex is not very high.

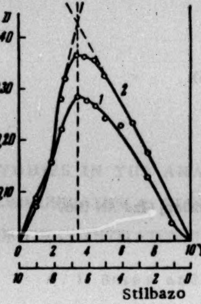

Fig. 3. Determination of the composition of the complex by the isomolar series method, using various concentrations of the reactants.
1) Total concentration $5.4 \cdot 10^{-5}$M;
2) total concentration $7.3 \cdot 10^{-5}$M.

The reaction studied was used for the photometric determination of yttrium in solutions of its salts in the absence and in the presence of lanthanum. In the latter instance, the yttrium and lanthanum were present in the solutions being photometrically measured, in the ratio of 1 : 1. The technique used was as follows. Into 25-ml standard flasks were introduced an ammonia—acetate buffer with a pH of 7.0, known amounts of a $3.4 \cdot 10^{-4}$ M solution of yttrium chloride, 1 ml of a 0.1% stilbazo solution, and the volume of the solution made up to the mark with the same buffer solution. A blank test was carried out in parallel. The optical density of the test solution was then measured with respect to the blank solution. For the determination of yttrium in the presence of lanthanum, 2 ml of a 20% acetone solution was added to the test solutions. The amount of yttrium was found by means of a calibration curve. The results (table) show that the reproducibility and accuracy of the method are quite good. Calculation of the mean arithmetic error, the mean, and the probable deviation of a single determination, was carried out on the basis of the results of six and seven determinations.

The optical density was measured on an FÉK-M photocolorimeter using a cuvette with a layer thickness of 0.5 cm.

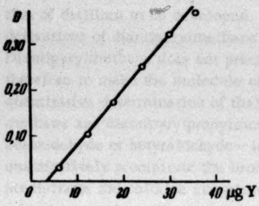

Fig. 4. The relation between the optical density of solutions of the complex and the amount of yttrium (μg per 25 ml).

SUMMARY

At a pH of 7.0 yttrium reacts with stilbazo while lanthanum does not. The reaction with yttrium was studied at this pH with the aim of using it for the phtometric determination of yttrium in the presence of lanthanum. The molar ratio of the reactants was established by the isomolar series method. The molar extinction coefficient was established using a liquid filter with maximum transmission at 540 mμ.

It has been established that lanthanum does not react with stilbazo at a pH of 7.0, but in the presence of lanthanum the optical density of solutions of the yttrium complex increases. This interference can be eliminated by adding a small amount of acetone to the test solutions. A study has been made of the effect of certain foreign ions and masking agents on the reactions of yttrium with stilbazo.

Yttrium has been photometrically determined with stilbazo both in the absence and in the presence of lanthanum. The results obtained show that the method has good reproducibility and accuracy.

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STUDIES IN THE ANALYTICAL CHEMISTRY OF THALLIUM

COMMUNICATION 4. DIANTIPYRYLPROPYLMETHANE AS A REAGENT FOR THE QUANTITATIVE DETERMINATION OF THALLIUM*

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In a previous article [1] it was shown that trivalent thallium in the presence of bromine ions is quantitatively precipitated by diantipyrylmethane. This permitted gravimetric and amperometric methods for the determination of thallium to be developed. The aim of the work described here was to study the possibility of using aliphatic derivatives of diantipyrylmethane for precipitating the bromide and chloride complexes of trivalent thallium. Diantipyrylmethane does not precipitate thallium quantitatively in the presence of chloride ions. It was of interest therefore to make the molecule of diantipyrylmethane heavier so as to obtain a selective precipitant for the quantitative determination of thallium in the form of its chloride complexes. For this purpose diantipyrylmethylmethane and diantipyrylpropylmethane were synthesized by condensing antipyrine with the appropriate aldehydes—acetaldehyde or butyraldehyde—in a hydrochloric acid medium. It was found that both these derivatives quantitatively precipitate the bromide complexes of thallium, but only diantipyrylpropylmethane quantitatively precipitates the chloride complexes; the latter reaction is characterized by high selectivity; accordingly all our subsequent work was carried out with diantipyrylpropylmethane.

EXPERIMENTAL

Synthesis of the Reagent. 5 g of antipyrine was dissolved in a small amount of water, and 2 ml of concentrated HCl and 2 ml of freshly distilled butyraldehyde added; the mixture was heated on the water bath for 30 minutes, after which it was diluted with water to 200 ml and neutralized with NH_4OH (1 : 1); at this stage an oily liquid appeared which crystallized rapidly. The diantipyrylpropylmethane, on recrystallizing from methanol had a m.p. of 155-156°. The yield was almost quantitative. A 1% solution of the reagent in acetic acid (1 : 1) was used for gravimetric determinations.

A solution of the sulfate of trivalent thallium was used in the course of the work; the concentration of this solution, established by a complexonometric method [2], was found to be 0.742 mg Tl/ ml.

In order to isolate, in an individual form, the products of the precipitation of the chloride (bromide) complexes of trivalent thallium with diantipyrylpropylmethane, the following procedure was adopted: To a solution containing 20-30 mg of trivalent thallium was added 5-10 ml of concentrated HCl (HBr) and 6-8 ml of a 1% solution of the base; after coagulation the precipitate was filtered off, washed a few times with water and then recrystallized from an alcohol—acetone mixture. When this procedure was adopted, a compound with a faint yellow color and which had a m.p. of 56-57° was isolated from the solutions containing chloride ions, while from the solutions containing bromide ions, the compound which separated out had a greenish-yellow color and had a m.p. of 128-129°.

The solubility in water of the compounds obtained was determined. For this purpose the freshly prepared precipitates, carefully washed with water, were placed in a flask containing distilled water, and shaken up in a thermostat for 5-6 hours until equilibrium was reached. After completion of shaking the solution was filtered.

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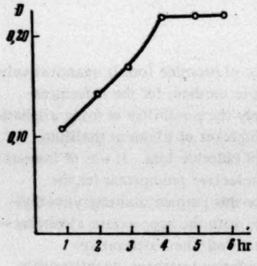
* For Communication 3, see Zhur. Anal. Khim. 14, 550 (1959).

TABLE 1

Solubility of the Compounds Obtained by Precipitating the Chloride (I) and Bromide (II) Complexes with Diantipyrylpropylmethane (20°)

Optical density of the extract		Tl content of 100 ml of a saturated solution		Solubility, M	
I	II	I	II	I	II
0,63	0,205	$1{,}08\cdot10^{-3}$	$1{,}36\cdot10^{-4}$	$5{,}3\cdot10^{-5}$	$6{,}6\cdot10^{-6}$
0,78	0,245	$1{,}24\cdot10^{-3}$	$1{,}64\cdot10^{-4}$	$6{,}1\cdot10^{-5}$	$8{,}0\cdot10^{-6}$
0,67	0,170	$1{,}15\cdot10^{-3}$	$1{,}12\cdot10^{-4}$	$5{,}6\cdot10^{-5}$	$5{,}5\cdot10^{-6}$
				Mean $5{,}7\cdot10^{-5}$	Mean $6{,}7\cdot10^{-6}$



The relation between the optical density of the extract and the time for which the precipitate of $C_{26}H_{30}O_2N_4\cdot HTlBr_4$ is shaken with water.

From the clear filtrate, 10 ml, in the case of the solution of the chloride compound, and 25 ml in the case of the solution of the bromide compound, were withdrawn, and 3 ml of a 0.1% KI solution, 3 ml of a 0.05% solution of diantipyrylpropylmethane, and 1 ml of 1 N H_2SO_4 added. The yellowish turbidity was extracted with 10 ml of benzene. The light absorption of the extracts was measured in an SF-4 spectrophotometer in a cuvette with a layer thickness of 10.0 mm, using a wavelength of 400 mμ. The amount of thallium was determined on the basis of a calibration curve constructed earlier [3]. The solubility found (Table 1) shows that both compounds, under certain conditions, can be used for the gravimetric determination of thallium.

Analysis of the compounds obtained showed that trivalent thallium is precipitated in the form of the tetrachloro- or tetrabromothallates of diantipyrylpropylmethane.

Found %: Br 34.53, 33.99; Tl 21.03, 21.87. $C_{26}H_{30}O_2N_4\cdot HTlBr_4$. Calculated %: Br 33.46; Tl 21.38.

Found %: Cl 19.72, 19.35; Tl 26.13, 26.59. $C_{26}H_{30}O_2N_4\cdot HTlCl_4$. Calculated %: Cl 18.23, Tl 26.28.

Thallium was determined by precipitating it and weighing it as TlI according to a method described earlier [1], while the halogens were determined by a mercurimetric method after decomposing an aliquot of the material, in a mixture of ethylene glycol and butanol, with sodium metal [4]. The somewhat high results for the halogens can be explained by the errors of the method when nitrogen is present in the organic material [5].

In order to establish the conditions for the gravimetric determination of thallium by precipitating and weighing it as $C_{26}H_{30}O_2N_4\cdot HTlBr_4$, a study was made of the effect of the bromide ion concentration and the acidity on the results. For this purpose the necessary amount of KBr (1.2 or 4 M) was added to a solution of a trivalent thallium salt; this was followed by 2-3 ml of a 1% solution of the reagent until no more precipitate formed. The total volume of the solution was 50 ml, while the acidity was 1 N with respect to H_2SO_4. After standing for a short time the precipitate was filtered off through a No. 3 glass crucible and washed, first with a 0.05% solution of the precipitant and then 2-3 times with water, and finally dried at 110-120°. From the results given in Table 2 it is clear that changes in the Br^- concentration from 0.1 to 1 M do not essentially affect the results for thallium. At a concentration of 2M for Br^-, precipitation of diantipyrylpropylmethane itself is observed; This explains the high results obtained.

It was also established that completeness of thallium precipitation is independent of the acidity of the solution (Table 3). Sulfuric acid was added to acidify the solutions.

TABLE 2

Effect of Bromide Ion Concentration on the Gravimetric Determination of Thallium in the Form of $C_{26}H_{30}O_2N_4 \cdot HTlBr_4$

KBr concn., M	Wt. of precipitate, mg	Thallium, mg		Error	
		taken	found	mg	%
0,1	34,2	7,42	7,31	−0,11	− 1,5
0,5	34,4	7,42	7,36	−0,06	− 0,8
0,5	34,8	7,42	7,44	+0,02	+ 0,3
1,0	51,4	11,13	10,99	−0,14	− 1,2
1,0	53,6	11,13	11,47	+0,34	+ 3,0
2,0	37,3	7,42	7,98	+0,56	+ 7,5
2,0	38,3	7,42	8,19	+0,77	+10,4

TABLE 3

Effect of Acidity on the Gravimetric Determination of Thallium in the Form of $C_{26}H_{30}O_2N_4 \cdot HTlBr_4$ (7.42 mg Tl taken)

H_2SO_4 concn., N	Wt. of precipitate, mg	Tl found, mg	Error	
			mg	%
0,1	34,7	7,42	0	0
0,1	34,4	7,36	−0,06	−0,8
2,0	35,6	7,61	+0,19	+2,5
2,0	34,2	7,31	−0,11	−1,5
5,0	34,9	7,46	+0,04	+0,5
5,0	35,6	7,61	+0,19	+2,5

TABLE 4

Effect of Chloride Ion Concentration and Acidity on the Gravimetric Determination of Thallium in the Form of $C_{26}H_{30}O_2N_4 \cdot HTlCl_4$

Concentration		Wt. of precipitate, mg	Thallium, mg		Error	
Cl^-, M	HCl, N		taken	found	mg	%
0,01	1,0	25,9	7,42	6,81	−0,61	−8,2
0,1	1,0	27,8	7,42	7,31	−0,11	−1,5
0,1	1,0	42,4	11,13	11,14	+0,01	+0,1
0,1	1,0	41,7	11,13	10,96	−0,17	−1,5
1,0	1,0	27,8	7,42	7,31	−0,11	−1,5
1,0	1,0	28,3	7,42	7,44	+0,02	+0,3
2,0	1,0	41,0	11,13	10,77	−0,36	−3,2
2,0	1,0	42,5	11,13	11,17	+0,04	+0,4
2,0	2,0	27,3	7,42	7,17	−0,25	−3,4
3,0	3,0	42,4	11,13	11,14	+0,01	+0,1
3,0	3,0	41,3	11,13	10,85	−0,28	−2,5
6,0	6,0	59,8	15,67	15,71	+0,04	+0,3
6,0	6,0	58,7	15,67	15,43	−0,24	−1,6

TABLE 5

Determination of Thallium in the Form of $C_{26}H_{30}O_2N_4 \cdot HTlCl_4$ in the Presence of Foreign Elements

Wt. of precipitate, mg	Tl taken, mg	Me added, mg	Tl found, mg	Error	
				mg	%
27,6	7,42	Zn 227+Cu 254	7,26	−0,17	−2,2
28,3	7,42	Zn 227+Cu 254	7,44	+0,02	+0,3
28,6	7,42	Zn 227+Cu 254	7,52	+0,10	+1,3
28,0	7,42	430 Bi	7,36	−0,06	−0,8
28,7	7,42	430 »	7,54	+0,12	+1,6
41,8	11,13	1000 Bi	10,98	−0,15	−1,4
28,6	7,42	540 Cd	7,52	+0,10	+1,3
28,1	7,42	207 Fe	7,38	−0,04	−0,5
58,9	15,67	15 In	15,47	−0,20	−1,3
34,8	9,40	97 In	9,15	−0,25	−2,6
35,9	9,40	165 In	9,43	+0,03	+0,3
35,6	9,40	100 Al	9,35	−0,05	−0,5
35,7	9,40	500 Na_2HPO_4	9,38	−0,02	−0,2
35,6	9,40	120 Mg	9,35	−0,05	−0,5
35,8	9,40	1000 Na_3AsO_4	9,41	+0,01	+0,1

A study of the conditions for the gravimetric determination of thallium as $C_{26}H_{30}O_2N_4 \cdot HTlCl_4$ was carried out in the same way as that described above, with the difference that, in view of the appreciable solubility of this compound in water, it was washed with a 0.05% solution of the precipitant containing 1M HCl, and then 2-3 times with 1 M HCl alone. The experimental results showed that neither the chloride ion concentration, starting at a concentration of 0.1 M, nor the acidity, within the limits 1-6 N, affect the completeness of thallium precipitation (Table 4).

It was also of interest to study the effect of foreign ions on the determination of thallium in the form of $C_{26}H_{30}O_2N_4 \cdot HTlCl_4$ and $C_{26}H_{30}O_2N_4 \cdot HTlBr_4$. Precipitation of thallium from bromide solutions by diantipyrylpropylmethane was carried out in a similar way to the precipitation of thallium with diantipyrylmethane described previously; the same ions were found to interfere [1]. Precipitation of thallium in a hydrochloric acid medium has, as was shown, a higher selectivity, since not only do zinc and copper not interfere with the determination but neither do cadmium (this metal is precipitated from bromide solutions), bismuth, and indium as long as the acidity is not less than 3M with respect to HCl. In order to determine thallium gravimetrically in the presence of Bi, In, and large amounts of Cd, the precipitate should be washed, first with a 0.05% solution of the reagent containing 3 M HCl, and then with 1 M HCl. The following do not interfere either: Al, Mg, Fe^{3+}, AsO_4^{3-}, PO_4^{3-}, (Table 5).

The following interfere: Ga, Sn^{4+}, Hg^{2+}, $Cr_2O_7^{2-}$, ClO_4^-, MoO_4^{2-}.

The method developed has been used for the determination of thallium in cadmium; an aliquot of cadmium (4-5 g) was dissolved in 10 ml of concentrated HCl; 1-2 ml of concentrated HNO_3 was then added to accelerate dissolution and to oxidize thallium to the trivalent state. The clear solution was diluted with an equal volume of water and a few ml of a 1% solution of the reagent added. The precipitate was filtered, carefully washed with a 0.05% solution of the reagent containing 3M HCl, and then with 1M HCl alone. The values found by the gravimetric method were 0.17 and 0.19% Tl, while by a complexonometric method [2] a value of 0.18% was obtained.

The method suggested for the precipitation of the chloride complexes of thallium by diantipyrylpropylmethane has a higher selectivity than the published method of precipitating thallium as $[(C_6H_5)_4As]TlCl_4$; in addition diantipyrylpropylmethane is not poisonous and is more readily accessible.

SUMMARY

Diantipyrylpropylmethane is suggested for the gravimetric determination of thallium: The latter is precipitated and weighed as $C_{26}H_{30}O_2N_4 \cdot HTlBr_4$ and $C_{26}H_{30}O_2N_4 \cdot HTlCl_4$. It has been established that the chloride complexes of trivalent thallium can be precipitated in the presence of Zn, Cu, Cd, Bi, In, PO_4^{3-}, and AsO_4^{3-}.

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A NEW REAGENT FOR LEAD

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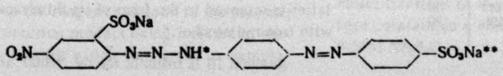
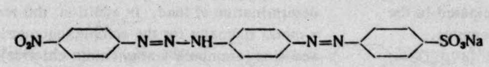
During a study of the analytical properties of sulfonated derivatives of cadion [1] (a reagent for cadmium), it was observed that the compound I, in contrast to compound II, gives a color reaction with lead [2].



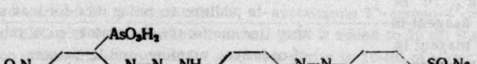
(I)



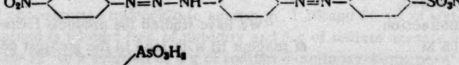
(II)

The capacity of I to react with lead is connected, presumably, with the presence of a sulfonate group in the ortho position with respect to the triazene group. Compound I, however, has no practical interest as a reagent for the photometric determination of lead. In order to obtain a more promising reagent for lead, it was decided to replace the sulfonate group in the ortho position with respect to the triazene group by other groups, which determine, according to published data, a quantitative reaction with lead ions. The first to be tried was the arsono group [4-6]. The comparative characteristics of the first compounds to be obtained (III, IV, V, and VI), as reagents for lead are given in the Table.

Compound III is the most interesting as a reagent for lead. In a solution of sodium tetraborate it gives with lead ions a stable colored compound; the graduation in the colors of solutions containing 1-10 μg of lead in 5 ml of solution is clear-cut in 1 μg intervals. The absorption curves are given in Fig. 1. The solution conforms to Beer's law (Fig. 2).



(III)



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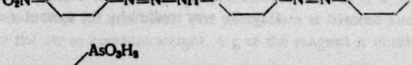

(V)

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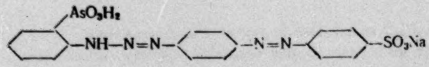
* On the structure of the triazine group, see [3]; we have arbitrarily left the double bond for those nitrogen atoms which belong to the original diazo compound.

** This reagent is issued by the chemical industry under the trade name "Cadion IREA".



$$C_6H_4(AsO_3H_2){-}NH{-}N{=}N{-}C_6H_4{-}N{=}N{-}C_6H_4{-}SO_3Na$$

(VI)

Copper, zinc, cadmium, nickel, lanthanum, uranium, cobalt, and manganese (II) form colored compounds with reagent III. The following elements do not form colored compounds with reagent III, and 50 μg of each of them does not interfere with the determination of lead: lithium, potassium, sodium, rubidium, cesium, magnesium, barium, strontium, calcium, arsenic, bismuth, tungsten, thallium (III), germanium, and gallium. The following elements do not form a colored compound with reagent III, but 50 μg of each of them interferes with the determination of lead: iron (III), aluminum, titanium, beryllium, tin (IV), tellurium, yttrium, scandium, zirconium, vanadium (V), molybdenum (VI), and thorium. One to ten μg of lead can be determined in the presence of the amounts indicated below of the following elements; 25 μg chromium, 25 μg tellurium, 25 μg yttrium, 10 μg aluminum, 10 μg beryllium, 10 μg tin (IV), 5 μg thorium and 2 μg scandium. 1 μg of each of the following elements interferes with the determination of lead: iron, titanium, zirconium, vanadium and molybdenum. Interference from up to 20 μg of Fe^{III} can be eliminated by addition of a 5% ammonium oxalate solution. In the presence of appreciable amounts of Fe^{III}, the latter is removed in the form of its thiocyanate by extraction with isoamyl alcohol.*

Characteristics of $2 \cdot 10^{-5}$M solutions of the Arsenic-Containing Compounds in 0.05 M $Na_2B_4O_7$ (pH about 9) Solution*

Compound	Sensitivity, μg Pb in 5 ml	Absorption max., mμ		Shift in the max., mμ
		in the absence of Pb	in the presence of Pb	
III	0,5	420	500	80
IV	1	420	480	60
V	5	410	430	20
VI	1	410	430	20

* M. P. Khoroshkaya participated in the spectrophotometric measurements.

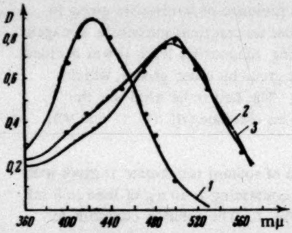


Fig. 1. Absorption curves of $2 \cdot 10^{-5}$M solutions at pH about 9. 1) Reagent in 0.05 M $Na_2B_4O_7$ solution; 2) reagent in 0.05 M $Na_2B_4O_7$ solution + Pb(excess); 3) product isolated from the interaction of the reagent with lead in 0.05 M $Na_2B_4O_7$ solution.

Reagent III is suitable for the visual and photometric determination of lead. In addition, this reagent can be used as a metal indicator for the complexonometric titration of lead and zinc (ammonia + ammonium chloride); a sharp color change is observed under these conditions ** [7].

The advantage of the new reagent for lead, as compared with the widely used dithizone, is that lead can be determined by means of III in the presence of other cations, using other masking agents which are much more convenient to use than potassium or sodium cyanide (e.g. thiourea for masking copper, potassium ferrocyanide for masking zinc). Moreover, the conditions under which the new reagent is used are simpler, since the additional reagents which are necessary for a determination of not require any special purification, as is the case when dithizone is used. The new reagent has already been tested in many organizations with positive results [8].

In addition to being used for lead and zinc, reagent III may find use for the determination of other cations, in particular, of cadmium, uranium, and lanthanum.

We have studied the products formed by the interactions of reagent III with lead in the greatest detail.

The molar ratio of reagent to lead during their reaction (Fig. 3) was studied by the isomolar series method [9].

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* The proportions indicated above, and the masking conditions were established by K. A. Smirnova.

** For examples and conditions of the use of the new reagent called sulfarsazin (Plyumbonon IREA) see intructions on its use (All-Union Scientific-Research Institute of Chemical Reagents). The reagent is now being issued by the chemical industry.

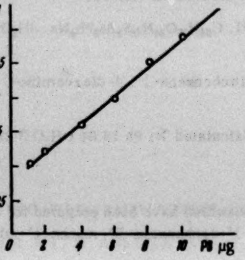


Fig. 2. Calibration curve. The optical density was measured on an FÉK-M apparatus fitted with a green filter.

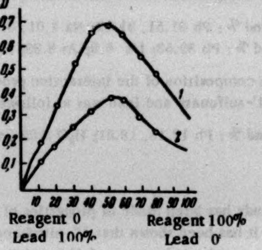
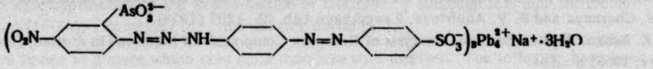
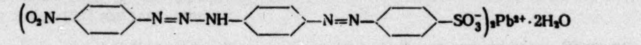


Fig. 3. Molar ratios during the interaction of reagent III with lead ions. 1) $2 \cdot 10^{-3}$M Pb and $2 \cdot 10^{-3}$M reagent; 2) 10^{-3}M Pb and 10^{-3}M reagent. The measurements were made on a SF-4 spectrophotometer at 500 mμ; the reagent solution hardly absorbs light at all in this region [10] (see Fig. 1). The total molar fractions of the components was kept constant in a volume of 25 ml of 0.05M $Na_2B_4O_7$.

The maximum on the composition—optical density curves corresponds exactly to a molar ratio of lead to reagent of 1 : 1. On the basis of an analysis of the interaction product formed between the reagent and lead in the presence of excess lead, the interaction product being isolated in the solid form, we obtained results which correspond to formula VII.



(VII)



(VIII)

It is obvious that the change in color of the reagent solution which occurs on addition of lead is determined by the interaction of the latter with the arsonium and triazene groups of the reagent. The interaction which is possible between lead and the sulfonate group does not lead to a change in color[*] and, accordingly, is not reflected on the curve relating optical density and composition of the solution. Interaction with the sulfonate group presumably occurs after saturation of the arsono group, i.e., in the presence of lead in excess of the reagent, and does not affect the accuracy of the photometric determination which is usually carried out in the presence of excess of the reagent.

Synthesis of 4"-Nitrobenzene-1", 4-diazoamino-1, 1'-azobenzene 2"-arsono-4'-sulfonic acid (mono sodium salt) (sulfarsazen). 2.62 g of 4-nitroaniline-2-arsonic acid is added to 20 ml H_2O and 10 ml 1N NaOH. To the solution is added a solution of 0.7 g sodium nitrite in 10 ml of water, and the whole poured into a mixture of 3 ml of concentrated hydrochloric acid (sp.gr. 1.18) and 60 ml of water. The solution of the diazonium compound obtained is filtered free of turbidity and 5 g of sodium acetate added to the filtrate. This solution is then added at 10-12° to a solution of 3 g of sodium 4-aminoazobenzene-4'-sulfonate in a mixture of 100 ml of alcohol and 200 ml of water. As the reaction proceeds, formation of a brick-red crystalline precipitate is observed. The reaction mass is kept for one hour. The precipitate is filtered and washed with 50 ml of alcohol. The paste obtained is dried in the air to constant weight. 4 g of the reagent is obtained.

Analysis of the preparation recrystallized from aqueous acetone (1 : 1) gave the following results:

Found %: Na 4.63; S 5.45, 5.27; N 14.72, 14.5; As[**] 13.00, 12.93. $C_{18}H_{14}N_6O_8NaAs$.
Calculated %: Na 4.02; S 5.6; N 14.69; As 13.09.

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[*] We established this point taking as an example compound II, which gave the interaction product VIII without any color change.

[**] Conditions for the determination of the arsenic content by a semimicro method were developed by N. A. Novikovskaya.

The composition of the interaction product (VII) of sulfarsazen and lead was as follows:

Found %: Pb 31.51, 31.79; Na 1.01, 0.98; As 8.61, 8.74; H_2O 1.91. $C_{54}H_{36}O_{24}N_{18}S_3As_3Pb_4Na \cdot 3H_2O$. Calculated %: Pb 32.53; Na 0.9; As 8.82; H_2O 2.12.

The composition of the interaction product (VIII) of sodium 4"-nitrobenzene-1", 4-diazoamino-1, 1"-azobenzene-4'-sulfonate and lead was as follows:

Found %: Pb 18.18, 18.01; H_2O 3.02. $C_{36}H_{26}N_{12}O_{10}PbS_2 \cdot 2H_2O$. Calculated %: Pb 18.94; H_2O 3.29.

SUMMARY

A study has been made of properties of arsenic-containing triazenes which have been prepared for the first time, and it has been shown that 4"-nitrobenzene-1", 4-diazoamino-1, 1'-azobenzene-2"-arsono-4'-sulfonic acid (sulfarsazen) can be successfully used as a reagent for lead.

It has been established by the isomolar series method that the maximum optical density is observed at a molar ratio of lead to reagent of 1:1.

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* See English translation.

PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF THORIUM WITH ARSENAZO*

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Of reagents suggested earlier [1-2] which give color reactions with thorium, the reagent thoron has already found wide analytical application [3-13]. The reagent arsenazo (uranon), which was described at the same time, has not yet found wide application for the determination of thorium**, although it is used for the determination of aluminum [14-15], zirconium [16], and the rare earths [17].

Many reagents are known at present which give color reactions with thorium. The following have been recommended: alizarin S [20], naphthazarin [21], 2-(p-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (SPADNS) [22], quinalizarin [23], p-dimethylaminoazophenylarsonic acid ("para-arsonic acid") [24], morin [26], pyrocatechol violet [27] and some others.

Of the reagents containing the AsO_3H_2 residue, the most interesting are thoron and arsenazo. These two reagents supplement each other. While thoron has the higher selectivity, arsenazo has a higher sensitivity.

The present article contains a description of a method which we have developed for the photometric determination of thorium by means of arsenazo.

Study of the Reaction Mechanism and the Conditions for Carrying Out the Reaction. Arsenazo (benzene-2-arsonic acid-<1-azo-2->1,8-dihydroxynaphthalene-3,6-disulfonic acid, sodium salt) dissolves in water to give rose-colored solutions. When thorium is present a blue-violet color develops or, when a large excess of thorium is present, a blue-violet precipitate forms.

The optimum pH for development of the thorium color lies in the range 1.8-2.0 (Fig. 1). The pH chosen in our work was 1.9.

The light-absorption curves of the solutions of the reagent and of the thorium complex are given in Fig. 2. The light-absorption curve of the solution of the complex was taken for solutions in which the reagent had been completely converted into the complex (on increasing the thorium concentration further the color does not change); the pH of 1.9 was established by adding a monochloroacetate buffer mixture to 10 ml of the weakly acid solution.

A wavelength of 580 mμ was chosen. On mixing the components the color develops almost immediately, and on standing for a further period in subdued light, it does not change for at least a month.

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* The work described was carried out in 1956.

** Recently, arsenazo under the name "neothoron" was used for the determination of thorium by some Japanese analysts [18, 19], who were apparently unaware of the work published by us earlier [1]. The method described in the present article differs essentially from the extraction method of the Japanese analysts, about which we learned when our work was completed

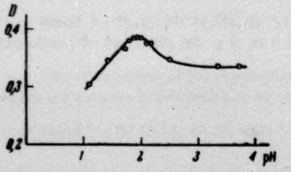

Fig. 1. Effect of pH on development of the color of the Th-arsenazo complex. $1.5 \cdot 10^{-3}$ M reagent solution. Cuvette 10 mm; λ= 572 mμ.

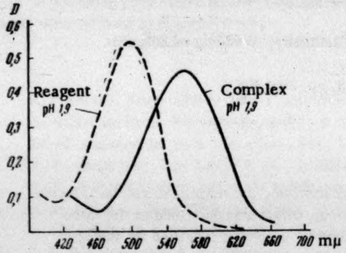

Fig. 2. Light absorption of solutions of the reagent arsenazo, and of its thorium complex. Reagent solution : $2 \cdot 10^{-5}$M . Solution of complex: $2 \cdot 10^{-5}$M reagent and $4.7 \cdot 10^{-5}$M thorium.

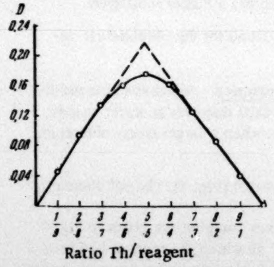

Fig. 3. Molar ratios by the isomolar series method. Solutions:Th) $1 \cdot 10^{-4}$M, arsenazo $1 \cdot 10^{-4}$M.

In the case of solutions with a pH of 1.9, in which the reagent present has been converted into the complex to the extent of 50%, changes of temperature in the range 20-35° do not exhibit an essential effect on the light absorption when the optical density is measured at 580 mμ.

By using the isomolar series method it was established that thorium interacts with the reagent at a molar ratio of 1 : 1 (Fig. 3). The pH of 1.9 was established by addition of a monochloroacetate buffer mixture.

The composition of the complex $[ThH_3R]^+$ and its instability constant were determined by Kuteinikov [28] who found that the constant was equal to $1.6 \cdot 10^{-16}$.

In the light of the ideas of intermolecular dissociation of cyclic salts [29,30] the mechanism of the color change in the case of the color reaction of thorium can be explained as follows. The color formed is determined by the corresponding ionic state of the residue of the colored molecule of the reagent in the thorium complex, which can be obtained even without the participation of thorium. This ionic state does not develop in an alkaline medium, in which a hydrogen ion splits off from the hydroxyl of the naphthalene nucleus. Accordingly, when the solution is made alkaline the rose color of the solution of the reagent does not change strongly. When, however, arsenazo is dissolved in about 94% H_2SO_4, in which salt formation of the nitrogen of the azo complex of thorium occurs, a violet-blue color develops similar to the color of solutions of the thorium complex (Fig. 4). This allows one to put forward the suggestion that the nitrogens of the azo group in the thorium complex are found in the same (ionic) state as in the case of the of the solution of the reagent in about 94% H_2SO_4, and this ionic state determines the color observed for the solution of the complex.

Sensitivity and Selectivity of the Reaction. On working with 0.00025 M solutions of reagent and a 10 mm cuvette, while the pH is 1.9, the addition of 0.1 μg Th/ml leads to a change of 0.006 in the optical density (SF-4 spectrophotometer, 580 mμ). Visual changes in color are not observable under these conditions, but they can be observed when a layer 20 mm thick is used.

The following elements: U^{IV}, U^{VI}, Pu^{IV}, Ti, Zr , Fe^{III}, Al, and certain other elements give violet colors of different shades with arsenazo at pH 1.9, in addition to thorium. Under the experimental conditions used, the alkali and alkaline earth elements do not cause any appreciable change in the color of the reagent. At pH 1.9 , the rare earths cause a change in color which is at least 1300 times weaker than that caused by thorium.

Fluorides, phosphates, sulphates, and other anions which strongly bind thorium prevent development of the color.

The characteristic effect of certain anions and cations is given in Table 1.

TABLE 1

Weight Ratios of Elements and Thorium for which the Experimental Error for Determination of Thorium Amounts to 5% (thorium concentration 1 μg, reagent concentration 0.0012%, pH 1.9)

Element	Ratio element : Th
Positive error	
Zr	0,14
Ti	1,0
Al	80
U^{VI}	200
Negative error	
F	0,16
P Phosphates	10
S Sulfates	80

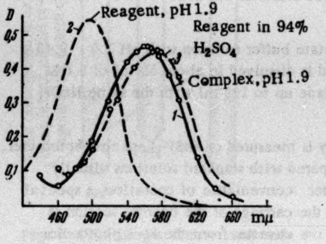

Fig. 4. Absorption curves for the complex at pH 1.9; for the reagent at pH 1.9 and in 94% H_2SO_4. 1) Solution of the complex: $1.9 \cdot 10^{-5}$M thorium and $2 \cdot 10^{-5}$ reagent at pH 1.9; 2) solution of reagent: $2 \cdot 10^{-5}$M at pH 1.9; 3) solution of reagent: $2 \cdot 10^{-5}$M in 94% H_2SO_4.

A convenient method for separating thorium from all other elements which affect the determination is precipitation in the form of oxalates. Since, when small amounts of thorium are involved, precipitation is incomplete [25, 31], it is necessary to resort to the use of a coprecipitant [6, 10], [32-34], the oxalates of the rare earths being suitable for this purpose [34].

Completeness of coprecipitation of thorium with rare earth oxalates was checked radiometrically. Coprecipitation was carried out as follows. The oxalates were precipitated by adding 20 ml of a 10% solution of $H_2C_2O_4 \cdot 2H_2O$ to 75 ml of a boiling solution of 0.3 N hydrochloric acid containing the rare earth elements and thorium labelled with UX_I*. After standing overnight the precipitates were filtered off, washed, dried, transferred to porcelain crucibles, ashed, and the residue calcined in a muffle. The amount of thorium coprecipitated was determined radiometrically.

After one oxalate precipitation, about 1.5-1.8% of the zirconium present is entrained in the precipitate. Accordingly, when the amount of zirconium present in the test material is more than twice the amount of thorium, the oxalate precipite must be reprecipitated.

After studying the effect of various factors on the separation and determination of thorium, the analytical method described below was developed. The results obtained when this method was used are illustrated by the examples given in Tables 3 and 4.

Determination of Small Amounts of Thorium with Arsenazo. (Applicable to silicate rocks).

The procedure outlined does not provide for zirconium contents of more than 0.5% and for titanium contents of more than 2% in the test material.

Reagents Required

1. 0.015% aqueous solution of arsenazo. This is prepared by diluting a 0.06% stock solution (0.15 g of the preparation is dissolved in 250 ml water).

2. A solution of rare earth nitrates containing 10 mg/ml of total rare earths, calculated in terms of the oxides. Two g of the oxides free from thorium** is treated with 10 ml HCl (1 : 1) on heating. The solution is evaporated on a water bath until the moist salts are obtained; the residue is dissolved in water and the volume made up to 200 ml with water.

3. Oxalic acid, 10% solution.

4. Wash liquor: 25 g of oxalic acid is dissolved in about 300 ml of water, 30 ml of concentrated HCl is added and the volume made up to one liter with water.

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* The UX_I was prepared by a method described in O. Hahn's book [35].

** In order to purify the rare earths from thorium, the solution of the rare earth nitrates is saturated with ammonium nitrate, and the Th extracted with methyl ethyl ketone. This operation is repeated six times. The rare earth hydroxides are precipitated from the aqueous phase with ammonia, the precipitate is then washed and finally calcined to the oxides.

TABLE 2

Effect of the Amount of Rare Earths on Completeness of Coprecipitation of Thorium. (The amount of UX_I taken gave a count of 2000-2100 cpm. The counter background was 18-24 cpm.)

Taken		Th coprecipitated, %	Taken		Th coprecipitated, %
*TR_2O_3, mg	Th, µg		*TR_2O_3, mg	Th, µg	
20	40,0	95	30	*	90
20	20,0	96	40	20,0	97
20	2,0	91	40	2,0	97
20	0,5	90	40	0,5	92
20	0,05	92	40	0,05	85
30	10,0	97			

* A solution of UX_I alone without addition of thorium was used.

TABLE 3

Determination of Thorium in Granites (sample weight 0.5 g)

Sample	Th added, µg	Th found, µg	Error in determining the Th added, µg
I	—	15	
I	11,5	28	11,3
II	—	20	
II	22	40	10,0
III	—	19	
III	30	48	3,4
VI	—	10	
VI	33	40	9,0

TABLE 4

Comparative Determination of Thorium in Granite and Clays by an Emanation Method and by the Suggested Method

Sample	Emanation method [36]**, 20 g of sample	By the suggested method, 0,5-1,0 g sample *
Granite 1	$2,2\cdot10^{-3}$	$2,1\cdot10^{-3}$
Clays		
I	$1\cdot10^{-3}$	$1,5\cdot10^{-3}$
II	$1,3\cdot10^{-3}$	$1,6\cdot10^{-3}$
III	$1,3\cdot10^{-3}$	$1,5\cdot10^{-3}$
IV	$1,5\cdot10^{-4}$	$1,6\cdot10^{-4}$
V	$8\cdot10^{-4}$	$6\cdot10^{-4}$
VI	$9\cdot10^{-4}$	$9,5\cdot10^{-4}$

* Determination of Th in granite was carried out by Yu. A. Balashev (GEOKhI, AN SSSR) and in clays by G. I. Malofeeva (GEOKhI, AN SSSR)

** Determinations carried out by K. G. Kunasheva (GEOKhI, AN SSSR).

5. Standard solution containing 5 µg Th/ml is prepared by diluting a stock solution with a concentration of 50 µg/ml [0.12 g $Th(NO_3)_4\cdot4H_2O$ in one liter of solution, which is standardized gravimetrically]. All solutions are about 0.02 N with respect to HCl.

6. Monochloroacetate buffer solution with pH 1.9 . 9.45 g of monochloroacetic acid is dissolved in about 50 ml of 0.1 M NaOH and the volume made up to 100 ml with the same NaOH solution.

The optical density is measured on an SF-4 spectrophotometer, or test solutions are compared with standard solutions visually. In the first case, for greater convenience of operation, a special cuvette holder placed in the carriage of the cuvette section is used; this enables one to use cuvettes from the M-1 photocolorimeter or from a universal photometer of the Pulfrich type. The construction of the cuvette holder is shown in Fig. 5.

The M-1 photocolorimeter itself can be used, but in this case a special filter is necessary.

Decomposition of Samples. Up to 2 g of finely ground material containing 1-10 µg of thorium is placed in a platinum dish, in which it is moistened with 1.5 ml of a solution of rare earth nitrates; 10 ml each of HF and HNO_3 is added and the mixture evaporated to dryness. Three lots of 10 ml of concentrated HNO_3 are added, the solution being evaporated to dryness each time. To the final residue is added exactly 3.7 ml of 6.0 M HCl and the whole heated, the solution transferred to a beaker and the volume made up to 75 ml (a mark made on the beaker).

Precipitation of the Oxalates. The solution obtained is heated to the boil and 20 ml of oxalic acid solution is added in small portions with stirring. After standing for an hour on the hot bath, 17 drops (0.5 ml) of the solution of the rare earth nitrates are added, and the solution left to stand for two hours.* The solution is poured through a filter while it is attempted

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* If after addition of oxalic acid the solutions have to be left overnight the solution of the rare earths can be added all at once—2ml (Point 1).

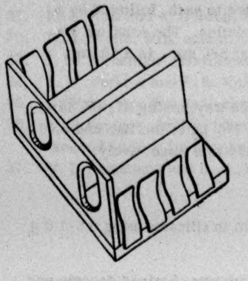

Fig. 5. Cuvette holder for the M-1 photocolorimeter for use with the SF-4 spectrophotometer.

to keep the precipitate in the beaker. The precipitate is washed 3-4 times by decantation using 20 ml each time. Any precipitate which has passed onto the filter is washed off the latter with a fine jet into the beaker with the main bulk of the precipitate; 3.7 ml of 6.0 M HCl is added and the mixture heated until the precipitate has dissolved. The volume is made up to 75 ml and the oxalates are precipitated again in the same way, but without adding any more rare earths; the solution is left to stand overnight. The residue is filtered, quantitatively transferred onto the filter, and then washed with wash liquor.

The second oxalate precipitation is carried out in order to separate any zirconium and titanium which have been entrained by the oxalates. When the Zr + Ti content of the test material is not more than twice the amount of thorium present, one oxalate precipitation is sufficient.

Wet Oxidation. The precipitate together with the filter is placed in a 100-ml quartz beaker, and 10 ml each of HCl, HNO_3, and $HClO_4$ added, the mixture is covered with a watch glass and heated on a grid until cessation of the turbulent reaction which occurs; the watch glass is removed and the $HClO_4$ fumes allowed to come off in the course of 15 minutes. The solution is evaporated down to 1-2 ml but not to dryness. It is then cooled and transferred to a 25-ml flask. The beaker is rinsed with water, and a few crystals (1-2 mg) of ascorbic acid added.

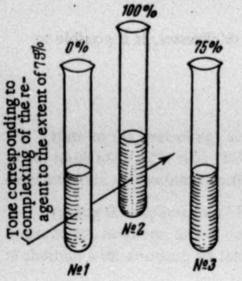
0%
100%
75%
Tone corresponding to complexing of the reagent to the extent of 75%
№1
№2
№3

Fig. 6. Obtaining a tone corresponding to 75% of the reagent bound as the complex.

Photometric Measurements. The solution is diluted with water to about 15 ml and ammonia is added until a slight turbidity is obtained; 1 M HCl is then added until the turbidity disappears, 4 drops (pH about 2) are finally added in excess. 1.25 ml of buffer mixture and 0.80 ml of reagent are added and the color which develops is compared with that of a reference in which the reagent is bound as the complex to the extent of about 75%. When the color of the solution being analyzed is more reddish than the color of the reference the volume is made up to 25 ml. In the opposite case another 0.60 ml of reagent is added from the same buret and the color agains compared with that of the reference*. If the color now proves to be redder than the color of the reference, the volume is made up to 25 ml and the solutions are compared. If even in this case again the color of the test solution is bluer than that of the reference, 2.6 ml of reagent solution is added, and the color compared again with the color of the reference. If it should now be redder than the color of the reference solution, the solution is diluted to 25 ml. If the opposite is the case an aliquot is taken from the solution being analyzed.

Depending on the amount of 0.00025 M solution of reagent taken (0.80, 1.40, and 4.00 ml) cuvettes with layer thicknesses of 50, 30, and 10 mm are taken and calibration curves Nos. 1, 2, and 3 used.

Preparation of a Reference Solution. Into two similar tubes are placed 0.2 ml of reagent (test tube No. 1) and 0.6 ml of reagent (test tube No. 2); 1.0 ml of buffer solution is added to each test tube, while into test tube No. 2, is added, in addition, sufficient thorium nitrate solution (50 μg Th/ml) to convert the reagent completely into a complex (100 % saturation of reagent with thorium [37]). No thorium is added at all to test tube No. 1. After the volumes have been made up to 20 ml, both test tubes are examined together (Fig. 6). Placed together in this way they give a color corresponding to "75% saturation".

Into test tube No. 3 is introduced an amount of reagent equal to the amount of reagent in test tubes Nos. 1 and 2 taken together. This is followed by a sufficient amount of the thorium salt solution so that the color of test tube No. 3 is the same as the total color of test tubes Nos. 1 and 2 taken together.

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* After addition of an increased amount of reagent the color intensity naturally becomes greater. Accordingly, the color of the test solution is examined in a thin layer while the flask is held at an angle.

Construction of Calibration Curves. Into a series of 25-ml flasks are introduced solutions containing 2.00, 4.00, 8.00, 16.00, and 32 μg of thorium; 2 ml of a solution of the rare earths is added to each, followed by a few crystals (1-2 mg) of ascorbic acid, 4 drops of 1 M HCl and 1.25 ml of buffer solution. The solutions are diluted to the mark and the optical density measured on a SF-4 spectrophotometer at 580 mμ in a 50 mm cuvette (calibration curve No. 1).

The other calibration curves, curves Nos. 2 and 3, were constructed in the same way, taking 35, 45, 55, and 65 μg of thorium and 1.40 ml reagent for curve No. 2, and 95, 120, 150, and 175 μg of thorium and 4.00 ml of reagent for curve No. 3, the cuvettes used having a layer thickness of 30 and 10 mm respectively.

SUMMARY

A method has been developed for determining $1 \cdot 10^{-4}$ and $1 \cdot 10^{-2}$% of thorium in silicates using 0.5-1.0 g samples.

A solution of rare earth nitrates is added to an aliquot of the sample and the mixture obtained decomposed with a mixture of $HF + HNO_3$; the dry residue is dissolved in 6 M HCl and the volume of the solution made up to 75 ml with water; oxalic acid is added and the thorium is coprecipitated with the rare earth oxalates. The operation is repeated twice. The oxalates are decomposed with a mixture of $HClO_4$, HNO_3, and HCl, arsenazo is added and photometric measurements are carried out at pH 1.9 (a monochloroacetate buffer mixture) on an SF-4 spectrophotometer at 580 mμ, or visually, using the standard series method.

By using three calibration curves and working in cuvettes with different layer thicknesses, it is possible to determine 1-175 μg of thorium without taking aliquots.

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Note to the preceding article. After the present article had been sent to the editor, S. B. Savvin [Doklady Akad. Nauk SSSR 127, 1231 (1959)] described a new, valuable and highly sensitive reagent for the photometric determination of thorium, namely arsenazo III.

During the separation of thorium by coprecipitation with the rare earth oxalates as discussed above, arsenazo III, however, is less convenient than arsenazo I, since the rare earths present during the determination of thorium with arsenazo III interfere to a considerably greater extent than is the case with arsenazo I.

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[*] Original Russian pagination. See C.B. translation.

A SENSITIVE AND SELECTIVE PHOTOMETRIC METHOD OF DETERMINING TITANIUM BY MEANS OF DISULFOPHENYLFLUORONE*

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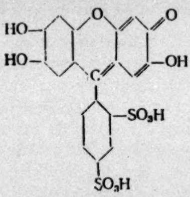
2, 3, 7-Trihydroxy-6-fluorone derivatives, substituted at the C_9 atom give color reactions [1] with titanium in a weakly acid medium, and can serve as reagents for its determination. One of the most widely used derivatives of trihydroxyfluorone —phenylfluorone—has already been suggested for this purpose [2, 3]. However, as a result of hydrolysis, most of the trihydroxyfluorone derivatives are precipitated at the high pH necessary for carrying out the reaction for titanium. The introduction of a sulfonate group into the trihydroxyfluorone molecule leads to the formation of a reagent which does not precipitate at any pH of the solution, and permits the sensitivity of the reaction to be increased appreciably. 9-(2',4'-Disulfophenyl)-2,3,7-trihydroxy-6-fluorone is a highly sensitive reagent of this kind for titanium,



This compound is obtained from triacetylhydroxyhydroquinone and 2,4-disulfobenzaldehyde, and is called disulfophenylfluorone for short. Its synthesis has been described before [4].

The sensitivity of detection of titanium by some trihydroxysulfofluorones is given in Table 1. The total volume was 5 ml, the reagent was added in lots of 0.2 ml in the form of a 0.05% alcoholic solution (50 mg of reagent and 0.5 ml of 6 N hydrochloric acid in 100 ml of 96% alcohol).

The molar extinction coefficients of solutions of the complexes formed between titanium and trihydroxyfluorone derivatives were determined at the optimum pH by the "saturation" method. The experiments were carried out at a limiting titanium concentration of $1\text{-}4 \cdot 10^{-6}$ g ion/liter and a constant concentration of the trihydroxyfluorone, while the ratio of titanium to reagent was varied from 1 : 2 to 1 : 8. The optical density was measured on a FMS-56 photometer with a light filter having a transmission region at 570 mμ, and using a 10 mm cuvette. A solution of the reagent of the same concentration as in the test solution was placed in a parallel cuvette.

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* Read at the analytical chemistry section of the VIII Mendeleev Conference on General and Applied Chemistry.

TABLE 1

Sensitivity of the Detection of Titanium by Trihydroxyfluorone Derivatives, and the Molar Extinction Coefficients of Solutions of their Complexes at 570 mμ

Trihydroxyfluorone, R at C_9	Optimum pH	Color		Limit of detection, Ti, μg/5ml	
		in the presence of Ti	of the control solution		
Propyl-	7,8	Rose-violet	Orange	0,5	52000
Trichloromethyl-	2	Violet	Yellow	0,3	60000
Phenyl-	2	"	"	0,5	50000
o-Hydroxyphenyl-	2	"	"	0,2	90000
o-Nitrophenyl-	2	"	"	0,5	70000
2,4-Disulfophenyl	6	"	"	0,05	108000

It is clear from Table 1 that many trihydroxyfluorone derivatives can serve as reagents for titanium, but the most sensitive of them is disulfophenylfluorone. This compound was accordingly chosen for the photometric determination of titanium.

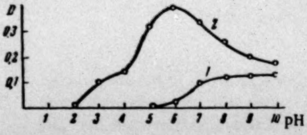

Fig. 1. Effect of pH on development of the color of titanium disulfophenylfluoronate solutions: 1) Reagent; 2) reagent + titanium (disulfophenylfluorone concentration $4 \cdot 10^{-5}$M, Ti concentration $12 \cdot 10^{-5}$ g-ion/liter; cell 10 mm;570 mμ).

In Fig. 1 is shown the relation between the optical density of solutions of the titanium disulfophenylfluorone complex and pH. The optical density was measured 30 minutes after the solutions had been prepared.

It is clear from Fig. 1 that the maximum optical density is observed at pH 6. At higher pH values the optical density of solutions of the reagent increases. Of the buffer solutions tested the most suitable proved to be a pyridine hydrochloric acid buffer, which was used in the subsequent work.

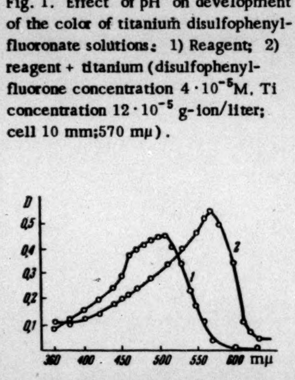

Fig. 2. Absorption curves. 1) Reagent; 2) reagent + titanium (disulfophenylfluorone concentration $2 \cdot 10^{-5}$M, Ti concentration $6 \cdot 10^{-5}$ g-ion/liter; cuvette 10 mm).

The absorption curves of solutions of disulfophenylfluorone and of the titanium complex at pH 6 were taken on a SF-4 spectrophotometer, the measurements being made in a 10 mm cuvette against water, 10 minutes after the solutions had been prepared. It is clear from Fig. 2 that the maximum absorption in the case of the reagent occurs at 500 mμ, while in the case of the complex it occurs at 570 mμ, where the reagent absorbs very little. Further measurements were accordingly carried out at 570 mμ.

The ratio of titanium to disulfophenylfluorone in the complex was established spectrophotometrically by the methods of isomolar series and molar ratios.

In the isomolar series method the solutions had a pH of 6. They were prepared by adding 0.6 ml of 10 N hydrochloric acid, 9-1 ml of a $1 \cdot 10^{-4}$ M aqueous solution of disulfophenylfluorone, and 6 ml of a 20% pyridine solution to 1-9 ml of a $1 \cdot 10^{-4}$ M solution of a titanium salt, and making the volume up to 25 ml in each case with water. The optical density of the solutions was measured when equilibrium had been reached, two hours after they had been prepared. The results obtained are given in Fig. 3.

The solutions for the molar ratios method were prepared in a similar fashion to that just described. Measurements were carried out by two variants: a) The concentration of disulfophenylfluorone was kept constant, while that of titanium was altered. The optical density was measured after two hours (the results obtained by this variant are given in Fig. 4). b) The concentration of the titanium salt was kept constant, while the concentration of the reagent was varied. These results are given in Fig. 5.

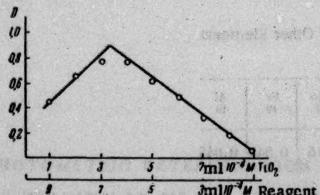

Fig. 3. Isomolar series method (the total concentration of the reactants was $4 \cdot 10^{-5}$M; cuvette 10 mm; λ = 570 mμ).

From Figs. 3, 4, and 5 it is clear that under the experimental conditions used, titanium forms with disulfophenylfluorone a complex in which the ratio Ti : Ph = 1=2.

Titanium disulfophenylfluoronate solutions conform to Beer's Law over a wide concentration range (Fig. 6). The titanium concentration was varied from 0.025 μg/ml to 1 μg/ml. The disulfophenylfluorone concentration was constant in all cases. The minimum of titanium which can be determined is 0.01 μg/ml. When excess reagent is present the color of the solution reaches a maximum after 10 minutes and remains constant for 12 hours.

Under the conditions used, germanium, tin (IV), antimony (III), zirconium, aluminum, iron, and molybdenum, as well as titanium, react with disulfophenylfluorone. Germanium, tin, antimony, and molybdenum can be masked with thioglycolic acid, while the others can be masked with sodium ethylenediaminetetraacetate. The optimum amounts of the masking agents are: 0.3 ml of a 10% solution of thioglycolic acid and 0.1-0.3 ml of a 10% solution of complexon per 5 ml of the final solution. Table 2 contains results obtained during the determination of titanium in the presence of some of the interfering elements, when the latter are masked with thioglycolic acid and complexon.

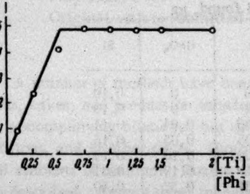

Fig. 4. Molar ratios method. Reagent concentration [Ph] constant (disulfophenylfluorone $2 \cdot 10^{-5}$M, the concentration of the titanium salt was varied from $0.1 \cdot 10^{-5}$ to $4 \cdot 10^{-5}$M).

We have used the disulfophenylfluorone method for the determination of traces of titanium in pure germanium and silicon. After the samples have dissolved, the germanium and silicon are readily removed, the first as its tetrachloride, the second as its tetrafluoride. The titanium is determined in the residue.

Germanium. One g of ground germanium is dissolved in a quartz flask in a mixture of concentrated hydrochloric and nitric acids, after which the germanium is distilled off with hydrochloric acid as described previously [5, 6]. The residue is transferred from the flask by means of 5 ml of hydrochloric acid into a 10- to 15-ml quartz beaker; 0.4 ml of a 0.5% solution of sodium chloride is added and the mixture evaporated to dryness on a water bath. The residue is transferred from the beaker into a colorimeter tube using 2 ml of 0.5 N hydrochloric acid.

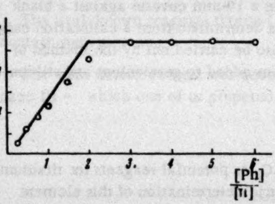

Fig. 5. Molar ratios method. Titanium concentration constant (concentration of titanium salt $2 \cdot 10^{-5}$M, concentration of the disulfophenylfluorone was varied from $0.1 \cdot 10^{-5}$ to $12 \cdot 10^{-5}$M).

Germanium Dioxide. 1 g of germanium dioxide is distilled in a quartz flask with 15 ml of 7-8 N hydrochloric acid. The residue is washed from the flask into a beaker by means of 5 ml of hydrochloric acid; 0.4 ml of a 0.5% sodium chloride solution is added and the procedure outlined above for metallic germanium followed.

Silicon. 1 g of ground silicon is dissolved in a platinum basin in 10 ml of hydrofluoric and 5 ml of concentrated nitric acid; the latter is added dropwise. The solution is evaporated to dryness on a water bath. The residue is moistened with 5 ml of 5% (by volume) sulfuric acid and evaporation continued untill all the sulfuric acid has been removed. 2 ml of hydrofluoric acid is added and the mixture evaporated to dryness on a water bath, 5 ml of a 0.1% solution of boric acid is added and again the mixture is evaporated to dryness on a water bath. The residue is washed into a colorimeter tube by means of 2 ml of 0.5 N hydrochloric acid.

Determination. To 2 ml of the solution obtained is added 0.3 ml of a 10% solution of thioglycolic acid, 0.1 ml of a 1% gelatin solution, 1 ml of a 0.025% alcoholic solution of disulfophenylfluorone (25 mg of reagent is dissolved on gentle warming in 100 ml of 96% alcohol), 1 ml of a 20% solution of pyridine, and 0.1 ml of a

TABLE 2

Determination of Titanium in the Presence of Other Elements (0.05 μg Ti taken)

Added, μg	Ge 50	Sn 10	Sb 10	Mo 10	Fe 10	Al 10
Ti found, μg	0,053	0,05	0,05	0,05	0,045	0,045

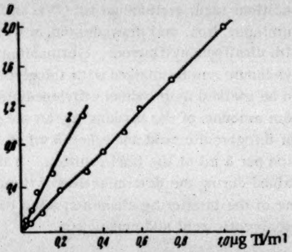

Fig. 6. Relation between optical density of solutions and titanium concentration: 1) Cuvette 10 mm; 2) cuvette 20 mm (disulfophenylfluorone concentration $6 \cdot 10^{-5}$M).

TABLE 3

Determination of Titanium in Germanium, Germanium Dioxide, and Silicon

Ti added, μg	Ti found, μg		
	Ge	GeO_2	Si
0	0	0	0,10
0	0	0	0,10
0,05	0,06	0,04	0,14
0,05	0,05	0,05	0,15
0,10	0,09	0,10	0,19
0,20	0,19	0,19	0,31
0,30	0,31	0,32	0,40
0,40	0,42	0,40	0,50
0,50	0,51	0,48	---

0.2% solution of sodium ethylenediaminetetraacetate, the solution being mixed after addition of each component. After 10 minutes the optical density of the solution is measured at 570 mμ in a 10-mm cuvette against a blank solution (the same solution but with no titanium). The amount of titanium is determined from a calibration curve which is constructed for the range 0.05-0.5 μg Ti. The determination can also be carried out by the method of standard series. Table 3 contains the results for the determination of titanium added to germanium and silicon; 1 g of each of the latter was used.

SUMMARY

A study has been made of trihydroxyfluorone derivatives substituted at C_9 as potential reagents for titanium; it has been shown that the most suitable of these derivatives for the photometric determination of this element is 9-(2', 4'-disulfophenyl)-2,3,6-trihydroxy-6-fluorone (disulfophenylfluorone). The ratio of titanium to disulfophenylfluorone in the complex is 1:2. Maximum light absorption by titanium disulfophenylfluoronate solutions occurs at 570 mμ, while the molar extinction coefficient is 108,000 at an optimum pH of 6. Solutions of the complex conform to Beer's law. The minimum amount of titanium which can be determined is 0.01 μg/ml. The method has been applied to the determination of traces of titanium in germanium and silicon; the sensitivity is $5 \cdot 10^{-6}$%.

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PHOTOMETRIC DETERMINATION OF MICROAMOUNTS OF URANIUM BY MEANS OF ARSENAZO III

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May-June, 1960
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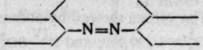
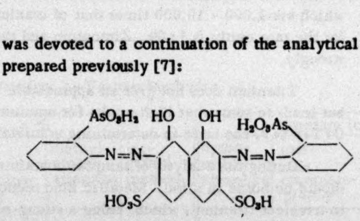
A number of methods have been suggested in recent years [1-3] for determining small amount of uranium in ores, cakes, and production solutions. As a rule, these methods assume preliminary separation of uranium from accompanying elements, but this is not always possible during control of production processes, under field conditions, and in other cases. Photometric methods have been those most widely used for the determination of small amounts of uranium. Dozens of reagents which give contrasting color reactions with U^{IV} and U^{VI} have been described. Among these reagents those which contain the group



are outstanding for their sensitivity.

The well-known reagents thoron I and thoron II [4, 6], and also arsenazo I (uranon) [4, 5] and arsenazo II [6] contain such a group.

The work described here was devoted to a continuation of the analytical application of a new reagent – arsenazo III – which one of us prepared previously [7]:



The synthesis and properties of the reagent have been described before [7].

The basic feature of arsenazo III which distinguishes it from other reagents described already is its capacity to form particularly stable inner-complex compounds with many elements, and these inner-complex compounds are not broken down in strong acids and in the presence of anions which usually mask the color reactions of elements: sulfates, phosphates, oxalates, and others.

Arsenazo III is not a specific reagent for uranium alone. Many elements under appropriate conditions (pH) give a color reaction with it. But, in strongly acid solutions, arsenazo III only reacts with those elements which form tetracharged cations [7]. Under such conditions the other elements do not interfere. Accordingly, with the aim of increasing the selectivity, despite some difficulties connected with the reduction and stability of quadrivalent uranium, the reaction of arsenazo III with uranium in precisely this valence state is used as the basis of the method suggested.

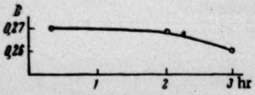


Fig. 1. Stability of solutions of the complex of U^{IV} and arsenazo III. Arsenazo III concentration 1.29×10^{-5}M; U^{IV} concentration 1.85×10^{-6}M. FÉK-M-1 photocolorimeter, red filter, 30-mm cuvette.

Of the reducing agents for uranium which we tested (thiourea dioxide, potassium iodide in a strongly acid medium, metallic bismuth, lead, and magnesium, various metal amalgams) granulated zinc in the presence of ascorbic acid gave the best results. The part played by ascorbic acid is the protection of quadrivalent uranium from oxidation by atmospheric oxygen.

Quadrivalent uranium reacts with arsenazo III to form a green complex; when excess reagent is present a mixed violet color of various shades is observed; the color of the reagent itself is rose,

The best results during colorimetric measurements are obtained when a 2-5 molar excess of reagent is used. This corresponds to violet and red-violet shades of the solution. The color is formed almost instantaneously and is stable for at least two hours (Fig. 1).

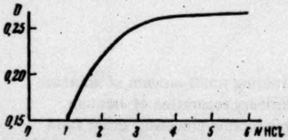


Fig. 2. Effect of acidity on the development of the color of the U^{IV}–arsenazo III complex. Arsenazo III concentration 1.29×10^{-5}M; U^{IV} concentration 1.8×10^{-6}M. FÉK-M-1 photocolorimeter, red filter, 30-mm cuvette.

It is clear from Fig. 2 that the color of the complex formed between quadrivalent uranium and arsenazo III in a strongly acid medium is constant over a wide acidity range.

The absorption curves of arsenazo III and of its complex with quadrivalent uranium are shown in Fig. 3. The molar extinction coefficient at 670 mμ, determined by the saturation method at a constant concentation of the reagent, is about 100,000.

When a FÉK-M-1 photocolorimeter was used in conjuction with a red filter and a 20 mm cuvette, the optical density was 0.030 for a uranium concentration of 0.04 μg/ml.

The effect showed by anions is small. For ratios of $U^{IV}: F^{-} = 1:25$, $U^{IV}: PO_4^{3-} = 1:10{,}000$, and $U^{IV}: SO_4^{2-} = 1:50{,}000$ the error in determining uranium does not exceed 5%.

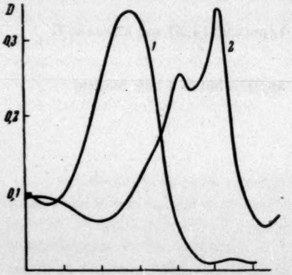


Fig. 3. Absorption of 1.3×10^{-5} M solutions of arsenazo III (1) and of the complex of U^{IV} with arsenazo III (2). Spectrophotometer SF-4, 10-mm cuvette.

A large number of cations do not interfere with the determination of quadrivalent uranium either, even when they are present in amounts which are 1,000 - 10,000 times that of uranium. The permissible ratio for the rare earths is 1: 60. Zirconium and thorium interfere quite strongly.

Titanium does not give an appreciable reaction with arsenazo III but leads to somewhat high results for uranium. For a weight ratio of U:Ti = 1:9, the error in determining uranium amounts to 5%.

During the analysis of samples containing titanium the following should be borne in mind. Metallic zinc reduces quadrivalent titanium to trivalent titanium, which, being a strong reducing agent, is capable of destroying the reagent. Accordingly, after treating the solution with zinc, the titanium should be oxidized with hydroxylamine hydrochloride.

Zirconium gives a reaction with arsenazo III which is similar to that of the latter with U^{IV}. Nevertheless, interference on the part of zirconium can be sharply decreased by carrying out the determination in the presence of oxalic acid, which strongly masks zirconium, and, to a markedly less degree, uranium (Fig.4). This means that it is possible to determine uranium in the presence of fairly large amounts of zirconium (Table 1).

Thorium exhibits the worst interference. When the amounts of uranium and thorium are of the same order, the following analytical procedure is possible: Prior to the reduction of uranium, thorium alone is determined [8], after reduction total Th + U^{IV} is determined, and the uranium content determined by difference.

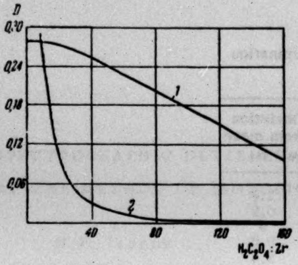


Fig. 4. Effect of oxalic acid on the development of the color of the complexes of quadrivalent uranium (I) and zirconium (II) with arsenazo III. Zr – 5 mg, U^{IV} – 0.02 mg.

Some of the results which illustrate the accuracy and reproducibility of the method developed are given in Tables 2 and 3.

Experimental Procedure. The calibration curve is constructed as follows: To seven small flasks containing 0, 4, 8, 15, 22, 30, and 38 µg of uranium are added 5-ml lots of 4 N hydrochloric acid, and some ascorbic acid (about 1.0 mg) added to each on the tip of a spatula, followed by 5-6 granules of zinc treated beforehand with hydrochloric acid. After 7-10 minutes the solutions are transferred to 50-ml standard flasks (the zinc is not transferred), the flasks being rinsed out with 4 N hydrochloric acid, 2 ml of a 0.05% aqueous solution of arsenazo III added, and the volume made up to the mark with 4 N hydrochloric acid; the optical density of the solutions is measured on a FÉK-M-1 photocolorimeter fitted with a red filter, using cuvettes with a layer thickness of 20 mm; the reference solution is a similar solution not containing uranium.

1.0-0.5 g of ore, ore cake, etc. is decomposed by heating with $HCl + H_2O_2$. The solution is cooled, diluted with 4 N HCl and transferred through a filter into a 100-ml standard flask. The volume is made up to the mark with 4 N HCl.

TABLE 1.

Determination of Uranium in the Presence of Zirconium (20 µg uranium taken. HCl concentration – 4N; $H_2C_2O_4 \cdot 2H_2O$ content – 80 mg; arsenazo III concentration 45×10^{-5}M; total volume – 50 ml)

Zr introduced, µg	U found, µg	Error, %	Zr introduced, µg	U found, µg	Error, %
—	20,1	+0,5	200	20,1	+0,5
20	20,0	0	400	20,3	+1,5
40	20,2	+1,0	700	20,9	+4,5
80	19,9	−0,5	1000	21,3	+6,5

TABLE 2

Determination of Uranium by Various Methods

Uranium found, %				Uranium found, %			
hydrosulfite-phosphate	partition chromatography	methyl violet-arsenazo	suggested method	hydrosulfite-phosphate	partition chromatography	methyl violet-arsenazo	suggested method
0,007	—	0,007	0,007	0,013	0,014	0,014	0,014
0,010	—	0,009	0,009	0,030	0,029	0,029	0,029
0,011	—	0,010	0,011	0,070	—	0,070	0,071
0,012	0,010	0,010	0,012	0,092	—	0,091	0,092

Two equal aliquots of 5 or 10 ml each are taken and transferred to small flasks. 1.0-2.0 mg of ascorbic acid is added on a spatula tip to each flask, while 5-6 granules of zinc are added to only one of the flasks. After 7-10 minutes the solutions are poured into 50-ml standard flasks (the zinc is not transferred); the flasks are rinsed out with 4 N HCl. Two ml of a 0.05% solution of arsenazo III is added to each flask and the volume made up to the mark with 4 N HCl. The optical density is measured on a FÉK-M-1 photocolorimeter fitted with a red filter, using cuvettes with a layer thickness of 20 mm; the solution which has not been reduced with zinc is used as the reference solution.

TABLE 3

Reproducibility of the Results Obtained during Determination of Uranium by the Method Recommended

Expt. No.	Uranium found, %	Deviation from mean, rel. %	Expt. No.	Uranium found, %	Deviation from mean, rel. %
1	0,0114	1,8	6	0,0119	2,6
2	0,0121	4,3	7	0,0115	0,9
3	0,0116	0	8	0,0116	0
4	0,0120	3,5	9	0,0115	0,9
5	0,0113	2,6	10	0,0112	3,5

The mean of ten determinations was 0.0116

When the test material contains zirconium, 2 ml of a 4% oxalic acid solution is added to each solution prior to addition of the reagent. The same amount of oxalic acid should be added to each of the solutions during construction of the calibration curve. The uranium content is found by means of the calibration curve.

SUMMARY

A rapid method for the determination of microamounts of uranium has been developed which is based on the formation of a colored compound between quadrivalent uranium and arsenazo III in a medium of 4 N HCl. Granulated zinc in the presence of ascorbic acid is used for reducing the uranium. The sensitivity of the method is 0.04 μg/ml. The limiting concentration of uranium which can be determined in test materials is 0.002%. Most of the accompanying elements, apart from thorium, do not interfere. Zirconium is selectively masked by means of oxalic acid.

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SPECTROGRAPHIC DETERMINATION OF URANIUM BY THE METHOD OF ISOTOPIC ADDITIONS

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It has been pointed out earlier [1-3] that the high accuracy and universal applicability of spectrographic methods of determining uranium are achieved by introducing known amounts of its rare isotopes U^{235} and U^{233} into the sample being analyzed. New variants of this method which ensure spectrographic results with an accuracy on the order of ± 1-2% are considered in the present article.

The Equal Blackening Method. The basic relation which is necessary for calculating the concentrations by the method of isotopic additions is the expression.

$$R_{85} = \left(\frac{1 - K + \frac{1}{n}\frac{C_5}{C_x}}{\frac{m_8}{m_5}\frac{C_5}{C_x} + K\frac{m_8}{m_5}} \right)^b . \quad (1)$$

where R_{85} is the relative intensity of the isotopic components of the analytical line; K is a coefficient which takes into account the U^{235} content of the natural element (about 0.007); n is the isotopic ratio of the preparation of the rare isotope used; C_8 and C_5 are the mass numbers of the isotopes b is a factor which takes into account the reabsorption effect; C_5 is the amount of the rare isotope added; C_X is the uranium concentration which it is required to determine and includes the light isotope U^{235} content of ordinary uranium.

From a consideration of relation (1) it follows that the method of isotopic additions, when one of the rare istopes of uranium is added to the sample, can be carried out by two methods: 1) Either a known amount of the rare isotope (C_5) is added to the sample, and the relative intensity (R_{85}) determined from the spectrogram obtained; or 2) the relative intensity R_{85} is assumed to be equal to unity, and the amount of the rare isotope C_5 which satisfies this condition for the given C_X is determined.

Both methods of carrying out the determination differ essentially from each other. In the first case, described by us previously [1, 2], in order to get correct results it is essential to take the background into account, and to establish excitation conditions which will guarantee the absence of reabsorption effects; it is also necessary to have the characteristic curves of the photographic emulsions used. Realization of all these operations is connected with overcoming a number of difficulties that limit the possibility of the method due to an experimental accuracy of ± 4-6%. In the second case there is no necessity for taking into account the background, reabsorption effects, and the properties of the photographic emulsion, as we shall show below. This makes it possible to improve the experimental results considerably with respect to both accuracy and repeatability.

Let us consider the basic positions of this method. Let C_5^0 be the amount of the light isotope for which the intensities of the isotopic components are equal. Then, if various amounts (greater and less than C_5^0) of the light isotope are added to several equal aliquots of the same sample, then the relationship between the difference in blackening of the components ΔS (= $S_8 - S_5$) and the relative concentration of the isotopes in the sample (C_5/C_X) will be in the form of a curve which intersects the axis of the relative concentrations.

It is not difficult to show that this relationship in the region where $\Delta S = 0$ can be represented by the equation

$$\Delta S = E\left(A - B\frac{C_5}{C_x}\right), \tag{2}$$

where

$$A = \frac{1 - K - K\dfrac{m_8}{m_5}}{\left(1 - K - \dfrac{K}{n}\right)\dfrac{m_8}{m_5}} \quad \text{and} \quad B = \frac{\dfrac{m_8}{m_5} - \dfrac{1}{n}}{\left(1 - K - K/n\right)\dfrac{m_8}{m_5}}$$

are coefficients which only contain calculated results, and are constant for the whole series of determinations carried out with a given preparation of the light isotope, while

$$E = \frac{\gamma b(1 - \beta)\lg e}{1 + \alpha + \beta}$$

is a coefficient which includes all the factors which depend on the actual conditions used for the analysis (γ is the contrast factor of the emulsion; α is the background intensity which is superimposed on the isotopic components and is expressed in terms of the fractions of the intensity of the component corresponding to the U^{238} isotope, i.e., $\alpha = I_b/I_8$; β is the intensity of the mutual overlapping of the isotopic components determined by the expression $\beta = I_{k5}/I_8 = I_{k8}/I_5$, where I_{k5} is the intensity of superposition of the "wing" of the U^{235} isotope component on the component of the U^{238} isotope, I_{k8} is the same for the component of the U^{235} isotope; and e is the base of natural logarithms.

Consideration of expression (2) shows that all the experimental curves constructed within the coordinates (ΔS, C_5/C_x) in the region where $\Delta S = 0$ (i.e., in the region of equal blackening of the isotopic components) will intersect the concentration axis independently of the value of the background (α), the contrast of the photographic emulsion (γ), reabsorption effects (c), and the position of this point being determined by the ratio

$$\frac{C_5^0}{C_x} = \frac{A}{B} = D. \tag{3}$$

Since, further, the sought for concentration C_x in all the aliquots of the test sample used for constructing a curve is constant, the latter can be constructed in the coordinates (ΔS, C_5) also. In this case the point of intersection of the curve with the concentration axis also gives, obviously, the sought for amount of the light isotope C_5^0, for which the intensity of the isotopic components is the same.

Calculation of the uranium concentration was carried out in this way according to the following formula, which is simple and suitable for calculation

$$C_x = \frac{C_5^0}{D},$$

where D is the value determined by the relation (3), and, is consequently, independent of the experimental conditions used.

From what has been said it follows that the method of equal blackening, when certain conditions are observed (absence of superposition of the lines of other elements or lines which enter into the composition of the molecular bands on the isotopic components; equality of the background superimposed on the isotopic components; a constant value for C_8/C_5 during the passage of uranium into the excitation region), should give the true uranium content of the sample with an accuracy which is determined only by the processes of measurement, i.e., by weighing (the operation of introducing the rare isotope into the sample) and by photometric measurements (measurement of blackening difference).

Since weighing can, in principle, be carried out with practical accuracy considerably greater than the required accuracy of the final result. the errors of the method of equal blackening are determined in the main by the photometric conditions. It is not difficult to evaluate the possible magnitude of this error. For this purpose let us consider the relation

$$\frac{dC_5}{C_5} = \pm \frac{1}{EA} d(\Delta S). \qquad (4)$$

which expresses the relation between the relative error of the final result and the value d (ΔS),which characterizes the accuracy of the process of photometric measurement.

The value d (ΔS) is obviously the smallest difference in blackening which the given emulsion and the given microphotometer are capable of recording. From a large number of measurements which we carried out on several microphotometers of the MF-2 type, it follows that the error d (ΔS) amounts to, on an average, ± 0.004. By substituting this value in formula (4) and assuming that we have the unfavorable case of a strong background ($\alpha = 1$, i.e., the intensity of the line is equal to the background intensity), we obtain a value of ± 1.0% for the relative error dC_5/C_5 (for $\gamma = 2$, $\beta = 0.1$, $n = 3.00$, $k = 0.007$, and $m_8/m_5 = 1.013$).

The method of equal blackening has been subjected to a large amount of practical verification. The work on the determination of a few percent of uranium (1-5%) carried out in conjuction with E.E. Batasheva, gave the following results: average reproducibility 1.2%, deviation between the results of the spectrographic method and a chemical method ± 2.2%; deviation between parallel determinations: for the spectrographic method 1.2%, for the chemical method 1.7%.

During the determination of tenths and hundredths of a percent the reproducibility was found to be ± 1.3%; the deviation between the results of the spectrographic and chemical methods was ± 1.6%.

In both cases samples of the most diverse composition were analyzed, the analysis being carried out on the basis of a single scheme.

During this work the main attention was given to establishing the possibility of using the method of equal blackening for the determination of uranium in ores. For this purpose a large number of ores differing with respect to their uranium content and to the composition of the enclosing rock was studied. It was shown that in the overwhelming number of cases there is no superposition at all on the 4244 A line, while the background to the components is the same and has an average value of $\alpha = 0.2$ ($\alpha_{\max} = 0.64$). A study of the character of the evaporation of the isotopes, the U^{238} which is contained in a natural sample of uranium, and the U^{235} which is artificially introduced into the sample, showed that their evaporation curves are identical for all the uranium ores examined. Thus, all the three above-indicated conditions, which are necessary for obtaining correct results are fulfilled in practice for all the uranium ores, independently of their composition and origin.

The Two Isotopes Method. In an earlier communication we have indicated the possibility of the simultaneous introduction of the two light isotopes of uranium into the test material [1, 2]. This method,which we have called the two isotopes method,permits one to count on obtaining results of satisfactory accuracy without taking into account the background, and on the basis of only one spectrum (or, more accurately, one aliquot of sample). This method is used to the greatest advantage in those cases where: 1) A rapid and accurate determination of uranium is required in samples of unknown composition and over a wide concentration range; 2) the tungsten lines superimpose and necessitate its separation from uranium (when the 4244 A line is used); 3) the sample contains large amounts of calcium, in which connection it is necessary to carry out a chemical separation of uranium and calcium by other methods; 4) the samples contain very small amounts of uranium and require preliminary chemical enrichment of the samples; 5) only a very small amount of material is available for analysis (e.g., a rare mineral). The basic principles of the two isotopes method are considered below.

The Optimum Amounts of the Isotopes to be Introduced. The amount of the light isotopes which are to be added simultaneously to the sample are determined by: 1) the photographic latitude of the emulsion; 2) the degree of enrichment of the preparations of the light isotopes. It is obvious that the isotope with the lower degree of enrichment should be added in the smaller amount. Assuming that $m > n$ (m is the degree of enrichment of the U^{233} isotope and n is the degree of enrichment of the U^{235} isotope), while $C_3/C_5 = 6$, where C_3 and C_5 are the concentrations of the light isotopes introduced into the sample, and assuming that $C_8^1 = C_5/n + C_3/m$ will not be greater than C_5, we obtain for the determination of m and n, the ratio:

$$\frac{m+6n}{mn} < 1, \text{ i.e., } m > \frac{6n}{n-1} \text{ (e.g., for } n=3, \text{ m should be} > 9).$$

When these conditions are fulfilled, the blackening of the heavy isotope in the spectrum of a sample to which the isotopes have been added will lie between S_5 and S_3, as long as the uranium concentration of the sample does not lie outside the limits of the region (C_5, C_3). In the examples given below, preparations of U^{235} with n = 3 and U^{233} with m = 16 were used; both isotopes were added to the samples in the form of standard nitric acid solutions.

Reproducibility of the Determination. To several aliquots of a sample containing 0.100% uranium were added 0.24% U^{233} and 0.042% U^{235}. In order to establish the reprodubility 11 aliquots were used, while the spectrum of each aliquot was scanned during exposure (1-2 minutes each). Determination of the concentration was carried out as follows.

The characteristic curve was constructed for the given emulsion within the coordinates (S, I). From this curve the values of I_8, I_5, and I_3 corresponding to the blackenings of the isotopic components S_8, S_5, and S_3 were found. The calibration curve was constructed for each exposure on the basis of the points corresponding to them (I_5, C_5) and (I_3, C_3); a straight line was drawn through these points. Table 1 contains results of the calculation of concentrations based on 48 spectra. Table 2 contains the results of the photometric measurements of several spectra.

For calculation, use was made of all the exposures in which the isotopic components of the analytical line U 4244 had appeared (49 out of the 60 spectra), independently of the value of the blackenings S_3 and S_5 (i.e., including small values of S_5 lying in the underexposed region, and large values of S_3 with a blackening density greater than 2.00).

Source of the Scatter of the Results Obtained. The basic sources of the scatter of the results presented are: 1) the use of the characteristic curves of the photographic plates; 2) the change in the background under the component of the U^{233} isotope as a result of the superposition of the "wing" of the band in the iron spectrum located on the the long-wavelength[*] side of this component; this is comparatively intense in some exposures (e.g. in Table 2, exposure 17); 3) strong differences in the blackenings of the components in the same exposure which lead to the appearance of local photographic effects (the most likely are development effects—the weak component of isotope U^{235} is located between the strong components of the U^{233} and U^{238} isotopes).

It is not difficult to show that in the second case low results are obtained, while in the third case high results are obtained. Both cases, when they are expressed to the strongest extent, can be easily detected from external signs and are left out of the calculations. Thus, as can be seen from Table 2, the very low result (0.086) occurs when the blackening of the iron band (S_{Fe}) is greater than or comparable to the blackening of the component of the light isotope U^{233} (S_3); a high result (0.106) occurs for very dense blackenings S_3 (greater than 2.00).

When one excludes from the results given in Table 1 all those results which are obtained during exposures for which $S_3 > 2.0$ and S_3 is approximately equal to S_{Fe} (10 of the 48 spectra belong to this category), then the mean reproducibility (of 39 spectra) increases and amounts to a value on the order of ± 2%. During further determinations carried out by the two isotopes method, exposures for which $S_3 > 2.0$ and S_3 is approximately equal to S_{Fe} were excluded for purposes of calculation. As for the first case, in principle it should be possible to eliminate this source of scatter by simultaneously introducing in known amounts, not two isotopes (as in our case), but three or more. In this latter instance there is naturally no need for constructing the characteristic curve of the photographic emulsion, and the calibration curves can be constructed directly on the basis of the blackenings, without converting them into intensities, whatever type of photographic materials are used. Another possible way is to study the nature of the relationship between the blackening curves and the type of emulsion, and to establish the physicochemical conditions under which the characteristic curve can be represented in the form $S = kI - \alpha$.

Determination of Uranium by the Two Isotopes Method in Samples Containing Calcium and in Production Wastes. When large amounts of calcium are present (about 15-30%) the U 4244 line is masked by the intense background from the resonance line Ca 4226. However, the line U 4244 can still be used even in these cases. We used two techniques for this purpose: fractional distillation of the sample during exposure, and the use of chemical methods of separation. The same techniques were also used for the analysis of some production wastes

[*] Inconsistency. See second note to Table 2-Publisher.

TABLE 1

Plate No.	Aliquot No.	Exposure No.	Found	Mean according to the exposure
		1	0,092	
		2	0,096	
7	1	3	0,096	0,095% (±0,002) (±2,0%)
		4	0,096	
		5	0,086	
	2	6	0,092	0,098% (±0,008) (±8,0%)
		7	0,106	
		8	0,100	
		9	0,099	
		10	0,099	
	3	11	0,100	0,099% (±0,002) (±2,0%)
		12	0,096	
		13	0,102	
		14	0,094	
		15	0,100	
		16	0,096	
9	1	17	0,086	0,097% (±0,005) (±5,0%)
		18	0,104	
		19	0,100	
		20	0,102	
		21	0,090	
	2	22	0,104	0,099% (±0,005) (±5,0%)
		23	0,100	
		24	0,100	
		25	0,099	
	3	26	0,096	0,098% (±0,002) (±2,0%)
		27	0,096	
		28	0,100	
		29	0,094	
		30	0,106	
	4	31	0,100	0,100% (±0,003) (±3,0%)
		32	0,098	
		33	0,104	
		34	0,100	
14	1	35	0,100	0,100% (±0,001) (±1,0%)
		36	0,100	
		37	0,100	
		38	0,101	
		39	0,100	
		40	0,096	
18	1	41	0,101	0,099% (±0,002) (±2,0%)
		42	0,101	
		43	0,096	
	2	44	0,101	0,099% (±0,003) (±3,0%)
		45	0,105	
		46	0,108	
5	1	47	0,099	0,102% (±0,003) (±3,0%)
		48	0,103	

Mean for all aliquots 0.099 ± 0.003 (±3.0%)

containing large amounts of tungsten. The concentration was calculated by the scheme set forth above; the final result was obtained by subtracting from the amount of C^{1}_{8} found the total amount of the heavy isotope U^{238} introduced into the sample together with the light isotopes U^{233} and U^{235}. The results are given in Table 3.

A consideration of the results given in Table 3 shows that the accuracy which can be obtained by the two isotopes method amounts to ±2% on the average; this is somewhat higher than the accuracy of chemical methods used for the analysis of poor ores and production wastes.

TABLE 2

Aliquot No.	Exposure No. *	Blackening of the isotopic components				Aliquot	Exposure	Blackening of the isotopic components			
		S_8	S_5	S_3	S_{Fe}**			S_8	S_5	S_3	S_{Fe}**
1	16	0,32	0,23	0,61	0,23	3	24	0,33	0,20	0,58	0,27
	17	0,42	0,24	0,82	1,07		25	0,42	0,25	0,77	0,19
	18	1,69	1,15	2.30	0,85		26	0,56	0,28	1,10	0,21
	19	0,27	0,17	0,53	0,28		27	0,60	0,29	1,08	0,31
2	20	1,25	0,68	2,00	0,54		28	0,35	0,23	0,62	0,30
	21	0,71	0,39	1,34	1,40	4	29	0,75	0,43	1,45	1,33
	22	0,56	0,28	1,06	0,14		30	1,52	0,91	2,18	0,81
	23	1,03	0,50	1,70	0,41		31	0,33	0,15	0,66	0,09
							32	0,76	0,42	1,30	0,23

*In accordance with Table 1.

**Blackening of the iron band located on the short-wavelength side of the U^{233} component.

TABLE 3

Analytical characteristics of the sample and the uranium according to chemical analysis	Isotopes introduced, %		Details of preliminary operations	Found by the two isotopes method
	U^{233}	U^{235}		
Slurry concentrate (0.07-0.08%), contains 0.05% tungsten	0.24	0.42	Fractional distillation of samples during exposure. Calculations were carried out on the basis of the last exposure free from the tungsten spectrum	0.083
			The sample was calcined after addition of the isotopes. It was then treated with HNO_3 (heating for 15-20 min). The solution was poured into dead rock and evaporated to dryness (calculations based on 1 aliquot, 3 exposures).	0.083; 0.088; 0.084 0.085; (± 0.002); (± 2.4%)
Mixed ore with 4.17 and 30% calcium. U^{238} 0.3%.	0.1	0.9	Exposure scanning in each case, 4% Ca	0.300; 0.315; 0.300
			Mean	0.305 (± 0.007; ± 2.3%)
			17% Ca	0.298; 0.300; 0.300
			Mean	0.303 (± 0.005; ± 2.0%)
			30% Ca	0.310; 0.300; 0.290; 0.285
			Mean	0.294 (± 0.008; 2.7%)
Carbonate ore, 0.07% (± 6%), contains 43.7% Ca	0.24	0.42	After addition of isotopes the sample was calcined and treated with hydrochloric acid. The residue dried in a porcelain basin was analyzed (one aliquot, four exposures)	0.072; 0.072; 0.074; 0.069
			Mean	0.072 (± 0.001; ± 1.4%)
Silicate ore 0.081% (± 6%)	0.12	0.42	After addition of isotopes the sample was calcined. Exposure scanning (one aliquot, five exposures)	0.078; 0.076; 0.076; 0.076; 0.077
			Mean	0.077 (± 0.001; ±1.4%)

TABLE 3 (continued)

Analytical characteristics of the sample and the uranium according to chemical analysis	Isotopes introduced, %		Details of preliminary operations	Found by the two isotopes method
	U^{233}	U^{235}		
Sand, 0.025% (± 30%)	0.10	0.05	Fractional distillation during exposure (two aliquots 4 and 6 exposures respectively)	0.034; 0.034; 0.034; 0.031
			Mean	0.033(± 0.001; ± 3.0%)
				0.033; 0.003; 0.032; 0.032; 0.034; 0.032
			Mean	0.033(± 0.001; ± 3.0%)
Cake, contains 0.07-0.09 uranium	0.24	0.42	Fractional distillation during exposure (one aliquot, four exposures)	0.086; 0.080; 0.084; 0.085
			Mean	0.084(± 0.002; ± 2.5%)

SUMMARY

A description is given of precision variants of the optico-spectrographical method of isotope additions which is used for the determination of uranium in ores and production wastes. It has been shown that by using the method of equal blackening, it is possible to eliminate the need for taking into account the background, the properties of the emulsion, and also reabsorption effects. The latter method permits determination of uranium in ores with an accuracy of ± 1-2%, independently of their uranium mineralization and the composition of the enclosing rock. The two isotopes method is discussed in detail. It has been shown that this method permits a rapid and fairly accurate determination of uranium in samples containing large amounts of calcium and tungsten, and also elements which are characterized by multilinear spectra (thorium, rare earths, etc.).

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THE USE OF SODIUM TUNGSTATE FOR THE TITRIMETRIC DETERMINATION OF IRON AND TITANIUM

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In developing a method for the determination of divalent iron in titanium slags containing di-, tri-, and quadrivalent titanium [1, 2], we used sodium tungstate as an indicator for the titration of the reduced titanium with potassium permanganate. The use of sodium tungstate permitted divalent iron to be determined in the presence of titanium, thanks to the considerable difference in the normal oxidation–reduction potentials:

$$E_0Ti^{IV}/Ti^{III} = +0{,}1v,\ E_0W^{VI}/W^{V} = +0{,}26v,\ E_0Fe^{III}/Fe^{II} = +0{,}77v.$$

Naturally, the question arises as to the possibility of using Na_2WO_4 as an indicator for the simultaneous determination of titanium and iron in titanium ores. Essentially, the method which has been developed reduces to the following: An aliquot of the ore is decomposed with a mixture of hydrofluoric and sulfuric acids. The quadrivalent titanium and the trivalent iron are then reduced with metallic cadmium to the tri- and divalent states respectively. Sodium tungstate is added to the solution after the reduction stage; reduction of W^{VI} to W^{V} by the trivalent titanium thereupon occurs.

In order to stabilize tungsten in the sulfuric acid solution orthophosphoric acid was used; this forms a compound $H_3[P(W_3O_{10})_4]\cdot(x+2)H_2O$, and in addition, sharply activates the reduction process of tungsten, shifting the oxidation–reduction potential of the system W^{VI}/W^{V} to the positive side [3]. The reduction product of tungsten, which has a blue color, is titrated with permanganate until the solution is colorless; divalent iron is then titrated in the same solution to the appearance of a stable pale-rose color.

There is a published reference [4] to the use of Na_2WO_4 for the determination of titanium and iron in ilmenite. The test material is decomposed with phosphoric acid. After addition of sulfuric acid and water, Ti^{IV} and Fe^{III} are reduced with a zinc amalgam and the solution is titrated with potassium permanganate in the presence of sodium tungstate until the blue color fixing the transformation $Ti^{III} \to Ti^{IV}$ disappears. Fe^{II} is then titrated to the appearance of a rose color.

We tried phosphoric acid as a solvent for titanomagnetite ores. The samples dissolved completely in the course of 15-20 minutes. All the same, phosphoric acid possesses a number of disadvantages which do not permit its use for decomposing the ores: 1)During reduction of Ti and Fe by metallic cadmium on heating, iron and titanium phosphate often separate out; 2) silicic acid, which separates out in a colloidal state during the decomposition process, clogs up the reducing agent, rendering it unsuitable for use. Consequently, we did not use phosphoric acid as a solvent, but merely for keeping the tungsten in solution.

To determine the amount of H_3PO_4 which is necessary to keep W in solution, but at the same time will not distort the titration results, a study was made of the effect of the amount of H_3PO_4 added on the separate

TABLE 1

Effect of Phosphoric Acid (sp.gr. 1.7) on the Determination of Titanium and Iron

H_3PO_4 added, ml	TiO_2, %		Fe,g		
	found	deviation	introduced	found	deviation
5	81,00	+0,17	0,00900	0,00900	0,00000
10	80,73	−0,10	0,00900	0,00906	+0,00006
15	80,85	+0,02	0,00900	0,00897	−0,00003
25	84,83	+0,40	0,00900	0,00630	−0,00270
30	88,63	+7,80	0,0258	0,0172	−0,0086

TABLE 2

Determination of Total Iron and Titanium in a Titanomagnetite Ore (Standard Sample 25 a, 13.42% TiO_2, 48.68% Fe total)

TiO_2 found, %	Deviation of TiO_2 from specified content, abs. %	Fe (total) found, %	Deviation of Fe from specified content, abs. %
13,41	−0,01	48,35	−0,33
13,42	0,00	48,72	+0,04
13,40	−0,02	49,29	+0,61
13,62	+0,20	48,30	−0,38
13,54	+0,12	48,54	−0,14
13,38	−0,04	48,18	−0,50
13,45	+0,03	48,55	−0,13

determination of mixtures of titanium and iron. A high-titanium slag containing 80.83% TiO_2 was dissolved by decomposing it in a mixture of HF + H_2SO_4. A standard iron solution was added to the solution thus obtained, after which Ti and Fe were reduced with metallic cadmium. Sodium tungstate and phosphoric acid were then added and the final solution titrated with potassium permanganate. The total volume of the solution was 200 ml. Results for the determination of titanium and iron are given in Table 1.

The results obtained show that in the presence of 5-15 ml of phosphoric acid titration proceeds normally (disappearance of the blue color is very clearly defined and occurs on addition of one drop of $KMnO_4$), while on addition of larger amounts of phosphoric acid (25-30 ml) the normal course of the titration is destroyed, and high results for titanium and low results for iron are obtained.

As V. S. Syrokomskii has shown, in the presence of excess phosphoric acid the oxidation–reduction potential of the system Fe^{III}/Fe^{II} decreases from +0.77 volt to +0.52 volt [5, 6], while the oxidation–reduction potential of the system W^{VI}/W^{V}, increases from +0.26 vol to +0.39 volt. Due to the drawing together of the potentials of iron and tungsten, Fe^{II} obviously starts to be titrated before the W^{V} is completely oxidized by the permanganate solution. Accordingly, we consider that titanium products must be decomposed in a mixture of sulfuric and hydrofluoric acids, while the amount of phosphoric acid added should not exceed 15 ml.

Two variants have been developed.

Variant 1. This variant is used when it is only necessary to determine total iron and titanium. 0.2-0.3 g of finely ground test material is moistened with water and is decomposed in a platinum basin with a mixture of 5-10 ml of hydrofluoric acid and 20 ml of sulfuric acid (1:1) on gentle heating. In order to remove the hydrofluoric acid the contents of the basin are evaporated until thick fumes of sulfur trioxide appear. The basin plus the decomposed sample are then cooled, 15-20 ml of distilled water is carefully added and the mixture heated to dissolve the salts. When the test material contains large amounts of calcium (e.g., in the case of perovskite), 5 ml of HCl (sp.gr. 1.19) is added to dissolve the $CaSO_4$. The contents of the basin are next transferred to a 300-ml beaker, the basin being rinsed out with a small amount of water so that the volume of the solution does not exceed 100-150 ml. Cadmium metal is added and the whole heated until the solution acquires a lilac color, after which it is passed through a cadmium reducer. The solution from the reducer is passed into a 500-ml receiver which is full of carbon dioxide and contains 5 ml of H_3PO_4 (sp.gr. 1.7) and 10-15 ml of water. If the sulfates formed during the decomposition have dissolved in the hydrochloric acid, then 25 ml of a Reinhardt mixture containing 3.5 ml of phosphoric acid is added to the titration flask. The total H_3PO_4 content of the solution,

TABLE 3

Determination of Total Iron and Titanium in Titanomagnetite Ore, Perovskite, and Sludge

Test material	Found			
	by titrating with $KMnO_4$, using $NaWO_4$ as indicator		On separate aliquots by the usual method	
	Fe total, %	% TiO_2	Fe total, %	% TiO_2
Titanomagnetite ore from the Kruchininskii deposit (Siberia)	25,83	8,22	25,69	8,20
	25,81	8,70	25,57	8,38
	25,72	8,74	25,48	8,69
Mean	25,8±0,04	8,6±0,2	25,6±0,1	8,4±0,2
Perovskite concentrate	5,05	44,57	4,97	44,58
	5,03	44,81	4,97	44,55
	5,00	44,73	4,97	44,81
Mean	5,03±0,02	44,7±0,1	4,97±0,00	44,7±0,1
Sludge from the decomposition of perovskite concentrate with nitric acid	5,77	64,16	5,64	64,39
	5,74	63,62	5,76	63,61
	5,86	63,96	5,85	64,09
Mean	5,79±0,05	63,9±0,2	5,75±0,07	64,0±0,3

amounting to 8.5 ml, does not affect the results for the determination of titanium and iron. The reducer is washed with a few portions of sulfuric acid (5:95). The final volume of the solution is 200 ml. To it is added 1 ml of a 5% aqueous solution of sodium tungstate; trivalent titanium is then titrated in a carbon dioxide stream with $KMnO_4$ solution until the blue color disappears, and the divalent iron is titrated to the appearance of a stable rose color.

Results of determinations carried out by means of variant 1 are given in Tables 2 and 3.

As is evident from the results in Table 3, the agreement between parallel determinations is good. The results obtained agree with the results obtained for iron using the method of reducing it with metallic bismuth with subsequent titration of Fe^{II} with $KMnO_4$ solution, while those obtained for titanium agree with results obtained for the latter by reducing titanium with metallic cadmium followed by titration of Ti^{III} with a ferric alum solution in the presence of NH_4SCN.

Variant 2. When it is necessary to determine di- and trivalent iron separately, Fe_{total} and TiO_2 are determined on aliquots which have been used for the determination of divalent iron. 0.3-0.5 g of finely ground test material is placed in a palladium flask, and moistened with a few drops of distilled water; 20 ml of sulfuric acid (1:3) and 5 ml of hydrofluoric acid are added, and the mixture is decomposed on heating in a carbon dioxide atmosphere for 20-25 minutes. Aliquots can also be decomposed as follows. The test material is placed in a platinum basin and 20 ml of sulfuric acid (1:1), 10 ml of hydrofluoric acid, and sufficient water to make the total volume up to 50 ml added. The platinum basin is covered with a glass lid which is the cut upper part of a wash flask. In the neck of the flask is placed a stopper with one hole, through which passes a glass tube (connection to a Kipp's apparatus supplying carbon dioxide), so that its lower tip just touches the bottom of the basin. The carbon dioxide thereby passes through the whole depth of the solution and fills the space above the platinum basin. This simple apparatus allows one to follow the course of the decomposition, and, in addition, removes any danger of the oxidation of divalent iron.

When the test sample is difficult to decompose and it is necessary to increase the heating period, distilled water should be added to the flask from time to time to keep the volume constant at about 50 ml; concentration of the sulfuric acid is thereby avoided. On completion of the decomposition, the contents of the flask are cooled in a carbon dioxide stream, and 20 ml of a saturated aqueous solution of boric acid added to remove any free HF. The solution is transferred from the basin to a 500-ml titration flask. Divalent iron is titrated with permanganate solution to a pale-rose color. After the Fe^{II} has been determined, metallic cadmium is added to the flask, and the titanium and iron reduced by gentle heating for 10-15 minutes. The lilac color which is the result of the formation of trivalent titanium ions is not observed in the presence of fluoroboric acid. But it does not interfere with the reduction of titanium and does not show any effect during the titration of Ti^{III} with $KMnO_4$ using sodium tungstate as indicator. The procedure outlined above for variant 1 is then followed.

TABLE 4

Determination of Divalent Iron, Total Iron, and Titanium Dioxide in a Standard Sample of Ore No. 25 a and in a Titanomagnetite Ore (Kruchininskii Deposit)

Test material	FeO found, %	Deviation of FeO, absolute, %	Fe found, %	Deviation of Fe, absolute, %	TiO_2 found, %	Deviation of TiO_2, absolute, %
Titanomagnetite ore	27,97	−0,09	48,54	−0,14	13,46	+0,04
Standard sample No.25 a	28,27	+0,21	48,45	−0,23	13,38	−0,04
Specified content						
28.06 % FeO	28,10	+0,04	48,68	0,00	13,49	+0,07
48.68% Fe (total)	27,94	−0,12	48,75	+0,07	13,50	+0,08
13.42% TiO_2	27,90	−0,16	49,10	+0,42	13,68	+0,26
Titano magnetic ore Kruchininskii deposit	16,00		25,64		8,17	
	16,24		25,76		8,48	
	16,30		25,55		8,36	
Mean	16,2±0,1		25,7±0,1		8,3±0,1	

Results of determinations carried out by variant 2 are given in Table 4.

As is evident from Table 4, the results for the content of divalent iron, total iron, and titanium dioxide in ore No. 25 a show only small deviations from the specified contents of these components, and coincide within the limits of experimental error with the results for Fe_{total} and TiO_2 obtained by means of variant 1 (see Table 2).

The results for divalent iron, total iron, and titanium dioxide obtained for the titanomagnetite ore show good reproducibility and agree with the results for TiO_2 and Fe_{total} obtained by means of variant 1 (see Table 3). It should be pointed out that the standard sample of ore No. 25 a contains 0.71% V_2O_5. The vanadium was not removed beforehand but was titrated with titanium and iron. When this is done it is necessary to bear in mind that V^V is reduced by cadmium to V^{II} [7], and is oxidized by permanganate to the quinquevalent state. The reduced vanadium was titrated with iron after oxidation of titanium and tungsten. Corrections for vanadium were introduced during calculation of the iron content.

SUMMARY

A titrimetric method has been developed for determining FeO, Fe_2O_3, and TiO_2 on one aliquot of sample using sodium tungstate as an indicator. A determination takes one hour. The method gives satisfactory results.

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DETERMINATION OF CERTAIN MICROIMPURITIES IN HIGH-PURITY SELENIUM

COMMUNICATION 3*

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In a previous communication [1], neutron activation methods were described for the determination of a number of elements with comparatively short half-life periods in selenium. The present article contains a description of a method for the determination in selenium of a number of microimpurities which give comparatively long-life radioactive isotopes (silver, mercury, chromium, cobalt, indium, and calcium).

The nuclear characteristics and sensitivity of determination, calculated for irradiation with a neutron stream of 8.7×10^{12} neutrons /cm^2 for 15 days, for an induced activity towards the end of irradiation of 40 decays/second, are given in Table 1.

A series of papers have been published on the activation method of determining elements in various materials, silver in Na and K alloys [2], chromium in tungsten [3], cobalt in granites and diabase [4], indium in minerals [5], indium in aluminum and thallium salts [6], cobalt in iron [7], silver in nickel [8], cobalt in antimony [9], calcium and chromium in magnesium [10], silver in silicon [11], and selenium in silicon [12].

As in the first part of the work we used the standard method of activation analysis with radiochemical separation and purification of the test elements.

Samples and standards were irradiated in a nuclear reactor under identical conditions. After irradiation known amounts of solutions of the salts of the test elements were added to the sample as carriers; the elements were then separated and purified radiochemically.

The preparations whose activity was to be measured were prepared in the form of precipitates filtered on a dismountable glass filter. The activities of the isolated preparations were compared under identical counting conditions with the activities of standard samples, taking into account the chemical yield. The activity of the preparations was measured on a type "B" setup with an end counting tube SI-2B.

The technique of separating and purifying the test elements was developed and checked using labelled atoms. In the course of each determination the radiochemical purity was controlled by comparing the absorption curves for β-rays in aluminum for samples and standards.

After irradiation the selenium sample (about 0.5-1 g) was washed off with hot and slightly dilute hydrochloric acid (1:1) for removing possible contamination on the surface; solutions of the salts of the carrier containing 10-20 mg each of the test elements were added, and the selenium was dissolved by heating in the minimum amount of concentrated HNO_3, with subsequent careful evaporation of excess acid.

The residue was dissolved in 40 ml water, about 0.5 ml of concentrated HCl and 1 g of urea were added and the solution boiled, the AgCl precipitate was filtered, and 2.5 g of $N_2H_4 \cdot 2HCl$ per g of selenium added to the filtrate; concentrated HCl was added so that the final solution was 3 N with respect to HCl. The solution was boiled and the precipitate of elemental selenium which separated out was filtered off and discarded. In order

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[*] For communication 2, see Radiokhimiya 1, 717 (1959).

TABLE 1

Isotope	Fraction of the activated isotope in the natural mix.	Activation cross section, barns	Half-life period of the radio-isotope formed	Sensitivity of the determination, g
In^{113}	0,042	56	50 days	$1{,}5 \cdot 10^{-9}$
Co^{59}	1	24	5,3 years	$1{,}5 \cdot 10^{-9}$
Cr^{50}	0,044	2	26,5 days	$1{,}3 \cdot 10^{-8}$
Hg^{202}	0,298	3	44 "	$8 \cdot 10^{-9}$
Ag^{109}	0,481	2,8	270 "	$1{,}5 \cdot 10^{-8}$
Ca^{44}	0,021	0,63	152 "	$3{,}8 \cdot 10^{-7}$

TABLE 2

Sample No.	Ag %	Hg %	Co %	Cr %	Ca %	In %
1	$8 \cdot 10^{-6}$	$1{,}1 \cdot 10^{-3}$	$3 \cdot 10^{-6}$	$7{,}2 \cdot 10^{-5}$	$\leqslant 3{,}5 \cdot 10^{-5}$	$5{,}4 \cdot 10^{-7}$
2	$2{,}3 \cdot 10^{-6}$	$1{,}9 \cdot 10^{-3}$	$2{,}3 \cdot 10^{-6}$	$4{,}8 \cdot 10^{-4}$	$6{,}0 \cdot 10^{-5}$	$4{,}7 \cdot 10^{-7}$
3	$7{,}5 \cdot 10^{-6}$	$7{,}2 \cdot 10^{-5}$	$5{,}6 \cdot 10^{-7}$	$4{,}2 \cdot 10^{-6}$	$\leqslant 2{,}5 \cdot 10^{-5}$	$4{,}5 \cdot 10^{-7}$
4	$5{,}1 \cdot 10^{-6}$	$1{,}3 \cdot 10^{-3}$	$1{,}2 \cdot 10^{-6}$	$1{,}3 \cdot 10^{-5}$	$4{,}5 \cdot 10^{-5}$	$2{,}7 \cdot 11^{-7}$
5	$1{,}07 \cdot 10^{-6}$	$1{,}2 \cdot 10^{-4}$	$6{,}36 \cdot 10^{-7}$	$1{,}57 \cdot 10^{-5}$	$\leqslant 3{,}5 \cdot 10^{-5}$	$2 \cdot 10^{-6}$

to remove the radioactive selenium more completely, three portions of selenious acid each containing 20 mg selenium were added to the solution, and the elemental selenium precipitate separated and discarded.

Separation and Purification of Selenium. The AgCl precipitate was washed with hot 2 N HNO_3; and dissolved on the filter in 20% NH_4OH; AgCl was separated out by acificiation with nitric acid and boiling; the precipitate was filtered off and dissolved in 20% NH_4OH; a solution of $Fe(NO_3)_3$ containing 10 mg of iron was added. The precipitate of $Fe(OH)_3$ which separated out was filtered off and discarded.

The silver in the filtrate was reduced to the elemental state by means of glucose. The silver precipitate was centrifuged, washed with 5% H_2SO_4 and dissolved in concentrated HNO_3. The solution was diluted with water until the acid concentration was about 5% with respect to HNO_3, the silver was titrated with thiocyanate, and the precipitate was filtered off and the activity measured.

Separation and Purification of Mercury. To the filtrate after removal of selenium was added a silver salt containing 5 mg Ag, and HgS + AgS precipitated by means of H_2S. The solution was boiled and the precipitate of the sulfides centrifuged and boiled with 3 N HNO_3. The mercuric sulfide precipitate, after being centrifuged and then washed with 3 N HNO_3, was dissolved in the minimum amount of aqua regia, the solution was diluted to 40 ml with water, and the elemental sulfur was filtered off and the mercury cemented on copper on weak heating for about two hours. The mercury was distilled off by heating to 400°, the distillate was washed into a beaker of hot concentrated HNO_3 and the solution diluted with water. The solution was neutralized with 10% sodium hydroxide solution and mercury precipitated by means of $K_2Cr_2O_7$. The precipitate was filtered off on a dismountable filter; it was then dried and its activity measured. The chemical yield was determined by dissolving the precipitate in HNO_3 and titrating the mercury with potassium thiocyanate.

Separation and Purification of Calcium. After removal of mercuric sulfide the filtrate was neutralized with 10% NaOH. The precipitate of chromium hydroxide and cobalt and indium sulfides was coagulated by boiling and then filtered off. To the filtrate were added solutions of cobalt and iron salts each containing 5 mg of the respective element; the precipitates which separated out were filtered off and discarded. The filtrate was acidified with hydrochloric acid and evaporated to a volume of 20-25 ml, and solutions of barium and strontium salts each containing 10 mg of the respective element, and 4-5 g of $(NH_4)_2SO_4$ were added. The solution plus precipitate were boiled; the precipitates were then filtered off and discarded. By adding $H_2C_2O_4$ and neutralizing the solution with 10% NH_4OH, calcium was precipitated as its oxalate. The precipitate was coagulated by heating on a water bath and was then centrifuged, dissolved in a small volume of aqua regia and the solution evaporated

TABLE 3

Element	Contaminating element	Activity introduced, cpm	Residual activity with the separate precipitates, %	
Hg			HgS	$HgCrO_4$
	Se*	200 000	0	—
	Te*	50 000	0,06	0
	Ag*	30 000	0,4	0
	Co*	240 000	0,1	0
	Fe*	50 000	0,1	0
	Cs*	100 000	0,05	0
Ag			AgCl	AgSCN
	Se*	200 000	0,01	0
	Te*	50 000	1	0,02
	Hg*	30 000	0,2	0
	Co*	240 000	0,01	0
	Fe*	50 000	0	—
	Cs*	100 000	~0,01	0
Ca			CaC_2O_4 1st precipitate	CaC_2O_4 2nd precipitate
	Se*	200 000	0	—
	Te*	50 000	0	—
	Hg*	30 000	0	—
	Ag*	30 000	0	—
	Co*	240 000	0,05	0
	Fe*	50 000	~0,01	0
	Sr*	100 000	~0,01	~0,01
	S*	14 000	0,	0
	Cs*	100 000	0,1	0
Cr			$BaCrO_4$	$Cr(OH)_3$
	Se*	200 000	0	—
	Te*	50 000	0	—
	Ag*	30 000	0	—
	Co*	240 000	0,06	0
	Fe*	50 000	0,1	0
	Zn*	20 000	~0,01	0
	Hg*	30 000	0	—
	Cs*	100 000	~0,01	0
In			$In(OH)_3$ Before extraction	$In(OH)_3$ After extraction
	Se*	200 000	0	—
	Te*	50 000	0	—
	Ag*	30 000	0	—
	Co*	240 000	1	0
	Fe*	50 000	90	~0,01
	Zn*	20 000	0	—
	Hg*	30 000	~0,01	0
	Cs*	100 000	0	—
Co			$CoHg(SCN)_4$	CoS
	Se*	200 000	0	—
	Te*	50 000	0	—
	Ag*	30 000	0	—
	Cs*	100 000	0	—
	Fe*	50 000	~0,01	0
	Zn*	20 000	4	~0,01
	Hg*	30 000	0	—
	Cr*	10 000	~0,01	0

to dryness. The dry residue was dissolved in water, an iron salt containing 10 mg Fe was added, and $Fe(OH)_3$ precipitated by addition of 5% NH_4OH; the precipitate was coagulated, centrifuged, and discarded. CaC_2O_4 was precipitated again from the filtrate, and then filtered off on a dismountable filter; it was washed with hot water, dried, and the activity measured. In order to determine the chemical yield, the precipitate was dissolved in hot dilute H_2SO_4 (1 : 10) and the oxalate titrated with potassium permanganate.

Separation and Purification of Chromium. The precipitate of sulfides and hydroxide was washed with 2% $NaNO_3$ solution and dissolved in 2 N HNO_3. The solution was boiled to remove H_2S; 25% NaOH was then added until the solution gave a basic reaction; then H_2O_2 was added. The precipitate of cobalt and indium hydroxides was coagulated by boiling, it was then filtered, the filtrate was neutralized with nitric acid, and a solution of a zinc salt containing 20 mg of zinc, added, and Na_2CO_3. The solution was boiled to remove H_2O_2, and the precipitate filtered off and discarded. The solution was acidified with concentrated HNO_3 and boiled to remove CO_2, and a solution of $BaCl_2$ containing 100 mg Ba was then added. Barium chromate was precipitated by neutralizing the solution with 5% ammonia; the former was filtered off, washed with a 2% solution of NH_4NO_3, and dissolved on the filter in hot HCl (1: 1). The solution was diluted three times and the chromium reduced to its trivalent state by means of hydrazine hydrochloride. Chromium was liberated by the action of NaOH; the precipitate was filtered off, dissolved in hot 2 N HNO_3, and a $Fe(NO_3)_3$ solution containing 10 mg Fe and hydrogen peroxide added, and the solution was finally made alkaline with a 10% ammonia solution. The $Fe(OH)_3$ precipitate was filtered off and discarded. By adding barium chloride containing 100 mg Ba, $BaCrO_4$ was precipitated. The latter was filtered off, washed with 2% NH_4NO_3, and then dissolved on the filter in hot HCl (1: 1); the chromium was reduced to the trivalent state with hydrazine hydrochloride and the chromium precipitated with NaOH; the precipitate was filtered off, dissolved on the filter in the minimum amount of dilute HNO_3, and the chromium precipitated again with 5% ammonia solution. The precipitate was filtered off on a dismountable filter, dried, and its activity measured. In order to determine the chemical yield the precipitate was calcined at 900° to Cr_2O_3.

Separation and Purification of Cobalt. The precipitate of indium and cobalt hydroxides was washed with a 2% $NaNO_3$ solution containing 1% NaOH, and was dissolved on the filter in hot HNO_3 (1: 3). Ammonia was then added until there was a strong odor of the latter; this was followed by addition of H_2O_2. The $In(OH)_3$ precipitate was filtered off and CoS precipitated in the filtrate by means of H_2S. The precipitate was coagulated by acidifying the solution with acetic acid; it was then centrifuged, and dissolved in the minimum amount of HNO_3 (1: 1); the solution was diluted until its concentration was 1 N with respect to HNO_3, and the precipitate of elemental sulfur filtered off. To the filtrate was added excess potassium mercurothiocyanate and the solution allowed to stand in the cold for not less than two hours. The $CoHg(SCN)_4$ precipitate was centrifuged and dissolved by heating in 2 - 2.5 N HNO_3; HgS was precipitated with H_2S; this precipitate was filtered off and discarded. The filtrate was evaporated almost to dryness, the dry residue was dissolved in 10 ml of water and the solution acidified with acetic acid. To the solution was added 10 ml of a saturated solution of KNO_2 and the whole allowed to stand overnight. The precipitate of potassium cobaltinitrite was filtered off, washed with 10% KNO_2 solution acidified with acetic acid, and then dissolved in HCl (1: 1). The solution was diluted with water and made alkaline with 25% ammonia solution; CoS was then precipitated with H_2S. The precipitate was coagulated by acidication with acetic acid, and was then filtered off on a dismountable filter, dried, and its activity measured. The chemical yield was established by calcining the precipitate at 500-800°, treating the residue with concentrated hydrochloric acid, removing the excess acid, then treating the residue with concentrated H_2SO_4, and finally removing excess of the latter by evaporation, and calcining the residue at 500° to $CoSO_4$.

Separation and Purification of Indium. The $In(OH)_3$ precipitate was washed with 2% $NaNO_3$ solution and dissolved on the filter in 6 N HBr. To this solution was added $Fe(NO_3)_3$ solution containing 10 mg Fe, and the whole extracted twice with diethyl ether. The indium was twice re-extracted with equal volumes of 6 N HCl and the aqueous phase treated with a fresh portion of ether. Indium was precipitated by addition of 10% NH_4OH; the precipitate was filtered off, washed with 2% NH_4NO_3 solution, dissolved in 2 N HNO_3, and again precipitated with ammonia. The precipitate was filtered off on a dismountable filter, dried, and its activity measured. The chemical yield was determined by calcining the precipitate to In_2O_3 at 1100°.

Table 2 contains results of the analysis of a number of samples of pure selenium, while in Table 3 the distribution of the activity between the precipitates is given.

SUMMARY

A method has been developed for the radioactivation determination of microamounts of silver, mercury, cobalt, chromium, calcium, and indium in selenium. The experimental accuracy for individual elements is 10-30%.

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RADIOACTIVATION ANALYSIS OF SEMICONDUCTING SILICON BY MEANS OF A MULTI-CHANNEL γ-SPECTROMETER

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The widespread use of Geiger-Muller counters in laboratory practice for the identification of radioactive isotopes on the basis of their radiation, has led to considerable chemical complication of the radioactive analysis of semiconducting silicon. This complication is bound up with the purification–which is essential in this case prior to identification of the precipitates isolated– of the impurities present before radiochemical purity is achieved [1-5]. Prospects for simplifying the usual techniques of radioactive analysis are opened up by the use of a scintillation γ-spectrometer [5-7] for identifying the impurities.

The aim of the work described here was to develop a technique of radioactivation analysis for particularly pure silicon, in which the sample is chemically decomposed, and the activity is measured with a multi-channel scintillation γ-spectrometer. The impurities determined in the course of this work are listed in Table 1. They were selected from a number of elements which could be present in silicon during its production and purification (Zn, Ta, etc.), or are of interest as possible alloy additives (Au, Sb, etc.).

Analytical Technique. Samples weighing 1-0.5 g were irradiated for 1-2 days in quartz weighing bottles in the channel of a nuclear reactor with a flux of 8.7×10^{12} neutrons/cm^2·sec.

After the irradiation the samples of polycrystalline silicon were successively washed with concentrated nitric and hydrochloric acids and with water. Multi-crystalline samples were carefully pickled with a mixture of nitric and hydrofluoric acid and then washed with water. The samples were subsequently dissolved and each impurity isolated from a test aliquot.

A scintillation γ-spectrometer consisting of a NaI(Tl) crystal 40 × 40 mm, a FÉU-S photoelectron multiplier, and a 50-channel amplitude analyzer was used for measuring the activity. The energy resolution of the apparatus was 9% with respect to the γ-line of Cs^{137}. A more detailed description of the apparatus has been given already [8]. The calibration was carried out on the basis of the γ-lines of standards.

The method only requires isolation of the impurity (without further radiochemical purification), since the entrained part of the impurity does not have an essential effect on the result of the measurements of the activity, as long as the coprecipitated element does not possess γ-lines whose energy is close to that of the γ-lines of the test element. When, however, such near γ-lines are present it is possible for identifying the impurity to establish the half-life period on the basis of the separated lines by taking repeated photographs of the spectrum. Normally this was only done for identifying Sb^{122} and As^{76}, since their γ-lines almost coincide, while the probability of mutual entrainment during separation is high. Measurement of the half-life period made it possible thereby to calculate the fraction of the coprecipitated active impurity.

With the aim of cutting down on the time during preparation of the sources, a standard glass centrifuge tube containing the isolated active precipitate was placed directly in the γ-spectrometer; the β-radiation in these cases was completely absorbed by an additional aluminum filter. The lengthy operation of determining the

TABLE 1

Element determined	Isotope identified	Energy of the γ-line, mev	Group to which the isolated element belongs	Standard	
				for irradiation	for measuring the chemical yield
Mn	Mn^{56}; 2,6 hr	0,845	I	$KMnO_4$	$MnSO_4$
Cu	Cu^{64}; 12,8 »	0,511		$CuSO_4$	CuCNS
Zn	Zn^{69*}; 13,4 »	0,44	II	$ZnSO_4$	$Zn[Hg(CNS)_4]$
As	As^{76}; 27 »	0,55		Metal	Metal
Ga	Ga^{72}; 14,3 »	0,84	III	Metal	Ga_2O_3
Sb	Sb^{122}; 2,8 »	0,568		Sb_2O_3	Metal
Fe	Fe^{59}; 46 »	1,161,3		Metal	Fe_2O_3
Ag	Ag^{110}; 270 »	0,656		$AgNO_3$	AgCl
Ta	Ta^{182}; 111 »	0,885 1,12 1,19 1,22	IV	K_2TaF_7	Ta_2O_5
In	In^{114}; 49 »	0,192	V	Metal	In_2O_3
Sn	Sn^{113}; 112 »	0,393	VI	Metal	SnO_2
Ca	Ca^{45}; 152 »	—	VI	$CaSO_4$	CaO
P	P^{32}; 14,3 »	—		$Na_2H_2P_2O_7 \cdot 6H_2O$	$Mg_2P_2O_7$

chemical yield (chemical loss during analysis) was carried out in order to cut down the time taken for the analysis after measuring the γ-spectra.

The content of an impurity was calculated after reducing the value of the activity to the same time by means of the usual equation

$$M_{imp} = \frac{A_{imp} \; B_{standard}}{A_{standard} \; B_{imp}} \cdot M_{standard}$$

where M_{imp} and $M_{standard}$ are the masses of the impurity and the standard; A_{imp} and $A_{standard}$ are their activities; B_{imp} and $B_{standard}$ are their chemical yields. The values of the activities of the standards and the impurities were determined from their photographed spectra, as the area of the peaks corresponding to the same γ-line.

Chemical Separation Operations. After washing, the irradiated sample of silicon was transferred to a platinum basin, into which the carriers of the test elements had been introduced and evaporated with hydrofluoric acid beforehand. After the silicon had been added to the basin, concentrated nitric acid was added and the silicon dissolved on careful heating.

After the sample had dissolved completely, the solution was evaporated with concentrated sulfuric acid to the appearance of white fumes in order to remove excess HF. The residue was transferred to a standard flask and diluted.

The impurities, as indicated in Table 1, were divided into six groups, each of which was determined on a separate aliquot. During the separation of the impurities into groups, not only the chemical properties of the elements were taken into account, but also the half-life period of the isotope on the basis of which the impurity was determined. The final precipitates of all the elements were separated by centrifuging.

Group I. An aliquot of the solution of the impurities was transferred to a test tube into which had been introduced beforehand a solution of carrier containing 10 mg Mn. A similar operation preceded the separation of the elements in each group.

The manganese was precipitated with NH_4OH and a few drops of H_2O_2. The precipitate was separated by centrifuging and dissolved in 6 N HCl containing a few drops of H_2O_2. The solution was boiled to destroy the hydrogen peroxide and the manganese precipitated with potassium chlorate. This precipitate was washed with water, alcohol, and ether. The chemical yield of manganese was determined as follows: The MnO_2 precipitate was dissolved in concentrated H_2SO_4 and quantitatively transferred to a crucible. The solution was evaporated to dryness, then the residue was calcined at 500-600° an weighed.

Group II. Amount of carrier: Zn−10 mg; Cu−10 mg; As−15 mg. Zn. The hydroxides were precipitated from solution with ammonia, and were removed and rejected. A stream of H_2S was passed into the strongly ammoniacal solution and the CuS and ZnS which precipitated were separated. The precipitate of sulfides was washed with dilute 1:10 NH_4OH, and treated with 1 N HCl on warming. The solution containing Zn was removed, heated until there was no odor of H_2S and diluted twice with 2 N HNO_3. The zinc was precipitated in the form of its mercurothiocyanate and rapidly separated from the solution.

Cu. The CuS precipitate was washed with 1 N HCl and dissolved in aqua regia. After removing the sulfur the solution was evaporated twice with concentrated HCl for complete removal of HNO_3. Copper was precipitated as the thiocyanate after reduction with SO_2.

As. The solution containing sulfo salts of arsenic, after removal of zinc and copper sulfides, was treated with 6 N HCl. The As_2S_5 precipitate was washed twice with concentrated HCl on boiling, and dissolved in 6 N HCl containing a few crystals of $KClO_3$. After removing the sulfur, arsenic was precipitated with hypophosphite in the form of the metal.

Group III. Amount of carrier: Ga−15 mg; Sb−15 mg.

Ga. Ga was extracted from solution with diethylether saturated with gaseous HCl. The ether was removed by heating and the residue diluted with 0.3 N HCl. 0.2-0.5 g of NH_4Cl was added to the solution, and gallium hydroxide precipitated by means of a 20% pyridine solution.

Sb. The aqueous solution left after extracting Ga was heated in order to remove traces of ether, and quinquevalent antimony reduced to the metal with aluminum foil. In order to remove traces of aluminum the precipitate was washed twice with concentrated HCl on heating.

Group IV. Amount of carrier: Fe−10 mg; Ag−10 mg; Ta−10 mg.

Ag. Silver was precipitated in the form of its chloride. The precipitate was separated, dissolved in ammonia, and again precipitated with hydrochloric acid. The silver chloride was separated and washed with water, alcohol, and ether. In view of the decomposition of AgCl in air, in order to determine the chemical yield, the tube plus precipitate was dried to constant weight at 100-105°, and weighed prior to photographing the γ-spectrum.

Fe. Iron was precipitated as its hydroxide from the solution remaining after removal of AgCl, by addition of

TABLE 2

Element	Ga	Zn	Cu	As	Sb	Fe	Ta	Sn	Ag	In	Mn	Ca	P, for 1 g
Sensitivity, g	$5 \cdot 10^{-7}$	10^{-8}	10^{-10}	10^{-10}	10^{-10}	$5 \cdot 10^{-6}$	$5 \cdot 10^{-10}$	$5 \cdot 10^{-6}$	$5 \cdot 10^{-8}$	$5 \cdot 10^{-8}$	10^{-9}	$5 \cdot 10^{-7}$	$5 \cdot 10^{-9}$

TABLE 3

Element	Ga	Zn	Cu	As	Sb	Fe	Ta	Sn	Ag	In	P	Ca
Content, %	$<10^{-6}$	$4{,}6 \cdot 10^{-4}$	$4{,}9 \cdot 10^{-5}$	$<10^{-6}$	$<10^{-6}$	$<5 \cdot 10^{-2}$	$<5 \cdot 10^{-5}$	$<10^{-2}$	$<5 \cdot 10^{-5}$	$<5 \cdot 10^{-4}$	$7 \cdot 10^{-7}$	$3 \cdot 10^{-3}$

TABLE 4

Element	Radio-activation method	Spectro-graphic method
Cu	$4{,}9 \cdot 10^{-5}$	$2 \cdot 10^{-5}$
Fe	$<5 \cdot 10^{-2}$	$2 \cdot 10^{-4}$
Ca	$3 \cdot 10^{-3}$	$2 \cdot 10^{-3}$

ammonia. The precipitate was removed by centrifuging, and washed with 4 N NH_4Cl; the precipitate was dissolved in hydrochloric acid (d = 1.1) and the iron extracted with ether. The ether layer was separated. After removal of the ether, iron hydroxide was precipitated with ammonia from the residue diluted with water.

Ta. After extraction, the aqueous layer was acidified with H_2SO_4 and tantalum phenylarsonate precipitated on heating. The precipitate was separated and washed with a dilute solution of phenylarsonic acid, alcohol, and ether.

Group V. Amount of carrier: In—10 mg.

0.2 g NH_4Cl was added to the solution and the hydroxide precipitated by addition of ammonia using methyl red as indicator. The precipitate was washed with dilute 1 : 5 NH_4OH, and then dissolved in acetic acid. The undissolved part of the hydroxide was rejected. The sulfides were precipitated from solution with a stream of H_2S; these were then separated and treated with 3 N HCl. The undissolved part was rejected. Indium hydroxide was precipitated from the solution with ammonia. The final precipitates of all the impurities in groups II, III, IV, and V were washed with water, alcohol, and ether after their separation.

Group VI. Amount of carrier: Sn—10 mg.

Tin together with the other hydroxides was precipitated with NH_4OH. After washing the precipitate with 4 N NH_4Cl, it was dissolved in 6 N HCl to which a few drops of H_2O_2 were added. After decomposing the peroxide by boiling, the solution was diluted twice and the tin precipitated with phenylarsonic acid. The precipitate was separated and washed with dilute phenylarsonic acid solution, an alcoholic solution of NH_4Cl, and ether.

The chemical yield of Cu, Zn, As, and Sb was determined from the difference between the weight of the tubes plus the precipitates, and the weight of the empty tubes dried to constant weight at 105-110°. In order to determine the chemical yield of Ga, Ta, Sn, In, and Fe, the precipitates were transferred to crucibles and calcined to the higher oxides at 900-1000°.

Standards. Aliquots of the standards after irradiation were dissolved in a suitable solvent and diluted to the mark in a standard flask. In order to decrease the effect of adsorption on the glass of the flask on the accuracy of preparing the source-standard, during the dissolution process an aliquot of the inactive salt of this element was added. During preparation of the source-standard, in order to photograph the γ-spectrum, an aliquot of the standard solution containing from 2×10^{-8} to 3×10^{-4} g of the irradiated material was added to the solution of the carrier. The amount of carrier chosen was such that the volume of the precipitate of the standard in the centrifuge tube was equal to the volume of solution obtained during the removal of the impurities from the sample. The standards were precipitated in the same chemical form as the impurities.

Phosphorus and Calcium. The analytical method involving chemical decomposition of the sample was developed so that in addition to the γ-active impurities it was also possible to determine those elements which give β-active isotopes on irradiation. Of such elements, phosphorus and calcium were of interest to us. The phosphorus and calcium activity was measured on a SI-2B end counter, and accordingly, after their separation a careful radiochemical purification was carried out. In calculating the content of the element, formation of additional amounts of P as a result of the fission of Si^{31} was taken into account [2].

Results. The absolute sensitivity of the determination (Table 2) was calculated by means of equation (1). The minimum value of the activity of the impurity which can be reliably measured was accepted as being equal to four times the value of the fluctuation of the cosmic background of the apparatus on the part of the spectrum corresponding to the peak of the photoelectron absorption of the main γ-line of the impurity being determined. The values of the activity and the mass of the standard were taken from the analytical results. In addition, during calculation, it was assumed that the first measurement of the activity of any impurity was carried out 12 hours after completion of the irradiation, and that the chemical yields for impurities and standards were approximately the same. In the case of P, the minimum activity of the impurity was determined as the activity of P^{32} formed from silicon during irradiation of an aliquot of 1 g. The calculated values of the sensitivity were checked for Zn Cu, As, Sb, and Ta by preparing sources with a given content of the elements. The check gave satisfactory agreement. The low chemical yield of the separation operation, and the certain amount of coprecipitation of the impurities which occurs in practice usually lower the sensitivity but not by more than one order.

Results of an analysis of a sample of semiconducting silicon are given as examples in Table 3. In order to check the technique used, the same material was analyzed in parallel by a spectrochemical method [9] in the Institute of Silicate Chemistry, Academy of Sciences, USSR. A comparison of the results is given in Table 4. The experimental error was determined by measuring a series of sources prepared with a known content of the elements, corresponding to their content in the test silicon (10^{-4} - 10^{-6}%). Zn, Cu, As, Sb, and Ta were chosen as the test impurities. The relative error was found to lie within the limits 10-40%.

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SUMMARY

A technique has been developed for the radioactivation analysis of silicon in which the sample is chemically decomposed; in this method, thanks to the use of a γ-spectrometer for measuring the induced activity of the impurities, the time taken to carry out an analysis is cut down significantly as compared with the time taken to measure the activity with a Geiger-Muller counter. This economy in time is made possible by the fact that the determination can be carried out without carrying out a radiochemical purification of the precipitates isolated, and by the fact that the majority of the impurities can be identified on the basis of one measurement of their activity.

The technique described is based on the determination, with high sensitivity, of impurities which give isotopes which become γ-emitters on being activated. However, in cases where it is necessary to determine elements which give isotopes which are pure β-emitters, the method can be extended by introducing the requisite procedures of radiochemical purification and using a Geiger-Muller counter.

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ANALYSIS OF CERTAIN ALLOYS BASED ON ZIRCONIUM

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Microamounts of aluminum, beryllium, magnesium, and some other elements cannot be determined photometrically against a background of zirconium. In order to separate zirconium from such elements the method of coprecipitating it with cupferron in an acid medium has been used [1-3]. However, in the presence of high contents of zirconium the bulky precipitate which is obtained always partially entrains the accompanying elements. In addition, removal of excess cupferron and its decomposition products from the filtrate presents some difficulty. These drawbacks can be overcome by extracting the zirconium cupferronates with chloroform. When such a technique is used other impurities (Fe, Ti, V, Nb, and Ta) which, like zirconium, interfere with the determination of Al, Be, Mg, and other elements, are extracted together with the zirconium.

The precipitated zirconium cupferronate belongs to the class of cupferronates which are weakly extracted by chloroform [4]. Furman et al. [5] have pointed out that such elements as tantalum, niobium, zirconium, etc., which are readily precipitated by cupferron in an acid medium, do not readily dissolve in organic solvents, while zirconium cupferronate is only moderately soluble in ethyl acetate. The basis for such a conclusion could be the fact that during extraction of zirconium cupferronate with chloroform (solid phase—liquid), separation of the phases into layers proceeds slowly, while on the boundary separating the organic and aqueous phases whitish films are obtained (the products formed by the decomposition of cupferron in an acid medium), which hinder a clear-cut separation of the phases. In other papers on the extraction of the cuferronates of various metals [6-11] zirconium, in general, is not mentioned.

We have established that in the presence of less than a 1.5 excess of cupferron, when the volume of chloroform is 10 ml, in a medium of 1 N H_2SO_4, the partition coefficient is about 500, i.e., when one extraction is carried out, about 0.2% of the zirconium remains in the aqueous phase. It is obvious that 2-3 extractions should ensure almost complete removal of zirconium.

Quantitative separation of zirconium form aluminum, beryllium, and magnesium is achieved by extracting zirconium cupferronate from 1 N sulfuric acid. This is the optimum acid concentration. An increase in acid concentration sharply depresses the extractibility of zirconium cupferronate. At an acididity less than 0.5 N, aluminum cupferronate is partially extracted.

Experiments showed that in a 1 N H_2SO_4 medium, when a 1.5 excess of cupferron was used, two extractions with chloroform ensured complete separation of 20-100 mg zirconium. A third extraction was carried out with pure chloroform (without cupferron) for purifying the aqueous solution from traces of cupferron and from its decomposition products. The most complete separation of zirconium was achieved when extraction of zirconium from 1 N H_2SO_4 was carried out with a chloroform solution of cupferron. In such cases the organic and water layers separated out rapidly, and no whitish films were formed on the phase boundary as is often the case after precipitation of zirconium with cupferron when the precipitate is dissolved in chloroform. Moreover, when such an extraction technique is used, pure nitrosophenylhydroxylamine passes into the chloroform layer, while the decomposition products of cupferron (which are not extracted by the chloroform) remain in the aqueous phase and thereby do not fall into the test solution after removal of the zirconium. Another advantage of this extraction technique is that the chloroform solution of cupferron is completely free from aluminum, magnesium,

TABLE 1

Determination of Al, Mg, and Be after Removal of Zirconium

Taken				Found, μg	Deviation		Taken				Found, μg	Deviation	
Zr, mg	Al, μg	Mg, μg	Be, μg		μg	%	Zr, mg	Al, μg	Mg, μg	Be, μg		μg	%
20	10	—	—	10	0	0	20	—	15	—	14	—1,0	—6,7
20	20	—	—	19,5	—0,5	—2,5	100	—	6	—	6	0	0
50	5	—	—	6,0	+1,0	+20	50	—	50	—	46	—4,0	—8,0
100	25	—	—	24,5	—0,5	—2,0	20	—	—	2,5	2,65	+0,15	+6,0
100	50	—	—	50	0	0	50	—	—	1,0	1,0	0	0
50	500	—	—	501	+1	+0,2	50	—	—	0,4	0,5	+0,1	+25
20	—	30	—	30	0	0	100	—	—	0,4	0,4	0	0

and other impurities which are not extracted by chloroform in an acid medium, as a result of which the optical density of the solution in the control experiment drops sharply and the sensitivity of the determination increases.

No aluminum, magnesium, and beryllium are lost under the conditions chosen. The chloroform solution of cupferron was prepared by adding 5 ml of a 5% solution of cupferron to 15 ml of 1.5 N H_2SO_4 in a separating funnel and shaking for two minutes with 10 ml chloroform. After the layers had separated the lower chloroform layer was transferred to another separating funnel, into which a solution containing 20 mg of zirconium and varying amounts of aluminum, magnesium, or beryllium had been introduced beforehand. After a period of shaking (1-2 minutes) when the layers had separated out, the chloroform extracted was poured off; then to the aqueous solution was added a second portion of a chloroform solution of nitrosophenylhydroxylamine, obtained by extracting a solution consisting of 15 ml of 1 N H_2SO_4 and 1 ml of a 5% cupferron solution with ten ml of chloroform. After the second extraction the lower chloform layer was removed and the aqueous solution extracted a third time with 5 ml of pure chloroform in order to remove cupferron decomposition products. For extracting 100 mg of zirconium the amount of cupferron added was increased to 20 ml of a 5% solution for the first extraction and to 5 ml for the second extraction. Aluminum was determined in the aqueous solutions remaining by means of aluminon, while magnesium was determined with titanium yellow [13], and beryllium with beryllon [14]. The zirconium content was controlled by means of pyrocatechol violet [12].

The results given in Table 1 show that on removing zirconium from aluminum, magnesium, and beryllium by extracting it with a chloroform solution of cupferron in 1 N sulfuric acid, no appreciable loss of the test elements is observed.

On the basis of this technique we have developed methods for the determination of aluminum, beryllium, uranium, magnesium, and zinc in alloys based on zirconium.

Determination of Aluminum. An accurately weighed aliquot of alloy (about 0.2 g) is placed in a platinum basin in which it is wetted with 10-15 ml of water and 2-3 ml of hydrofluoric acid in small portions. The basin is covered with a lid and is left to stand for several minutes until the alloy has dissolved. 1-2 ml of sulfuric acid (sp. gr. 1.84) is then added and the solution evaporated almost to dryness. The walls of the basin are washed with 3-5 ml of water and the solution again evaporated to dryness. To the dry residue is added 10-15 ml of water and 2.8 ml of sulfuric acid (sp.gr. 1.84) and the whole heated until the salts have dissolved completely; the solution is then transferred to a 100-ml standard flask and the volume made up to the mark with water. For removal of the zirconium, an aliquot of this solution containing from 20-100 mg of zirconium (10-50 ml) is transferred to a 150-200-ml separating funnel, and the solution extracted with a chloroform solution of cupferron as described above.

The aqueous solution left after removal of the zirconium is transferred to a quartz beaker and is evaporated until its volume is 2-3 ml; after cooling, 3-4 drops of hydrogen peroxide is added and the solution evaporated to dryness. To the dry residue is added 1 ml of 1 N hydrochloric acid, 5-6 ml of water, and the whole heated until the residue has dissolved completely. When the sample contains small amounts of aluminum (thousandths or

TABLE 2

Determination of Aluminum in a Zirconium Alloy

Sample wt., g	Aluminum determined, %	a -x	Sample wt., g	Aluminum determined, %	a -x
0,2004	0,120	+0,005	0,2036	0,123	+0,002
0,2060	0,121	+0,004	0,2029	0,133	—0,008
0,2038	0,132	—0,007	0,2096	0,119	+0,006
0,1900	0,122	+0,003	0,2008	0,129	—0,004
0,1938	0,134	—0,009	0,2000	0,129	—0,004
0,2073	0,125	0	0,1996	0,120	+0,005

$\bar{a} = 0.125$; mean square error $\sigma = \pm 4.4\%$ (relative); sensitivity of the method 0.01%.

hundredths of a percent), some idea of which can be gained from the small amount of dry residue, the solution obtained is transferred to a 50-ml standard flask and the aluminum determined photometrically. When the aluminum content amounts to tenths of a percent or to several percent, 2-3 ml of 1 N HCl (an accurately measured amount) is taken to dissolve the residue; the solution obtained is transferred to a 25-or 50-ml standard flask, and an aliquot of this solution containing up to 100 μg of Al transferred to another flask (50 ml). The solution should contain 1 ml of 1 N HCl. To the aliquot of solution is added 20 ml of water, 0.2 ml of 1% ascorbic acid, 2.5 ml of 0.1% aluminon* and the volume made up with a pH 4.5 buffer solution (27 g of sodium acetate and 11.3 ml of HCl per liter). The flask plus solution is left on a water bath for 10 minutes. After cooling, the optical density is measured on a photocolorimeter fitted with a green filter, using a layer thickness of 5 cm; the reference solution is prepared by introducing into a standard flask (50 ml) 19 ml of water, 1 ml of 1 N hydrochloric acid, 2.5 ml of aluminum solution and the volume made up to the mark with the buffer solution (pH 4.5). The aluminum concentration is determined by means of a calibration curve which is constructed by measuring the optical density of standard solutions containing 5, 10, 20 etc. up to 100 μg of aluminum. A control test is carried out with all the reagents used.

Table 2 contains experimental results for the determination of about 0.12% aluminum in an alloy containing zirconium.

Determination of Aluminum in the Presence of Beryllium. In the presence of beryllium (e.g., during the analysis of ternary alloys zirconium—aluminum—beryllium) the aluminum is removed beforehand by extracting aluminum 8-hydroxyquinolate with chloroform. The sulfuric acid solution obtained after removing the zirconium is netralized with ammonia until the medium is slightly acid (about 0.1 N); it is then heated, and, if necessary, it is evaporated to a volume of not less than 20 ml when it is transferred to a 50-ml separating funnel. To the hot solution (50-60°) is added 12 ml of a 5% acetate solution of 8-hydroxyquinoline,** small portions of 2 N sodium acetate solution are added until a permanent precipitate of aluminum 8-hydroxyquinolate is obtained. The solution plus precipitate in the separating funnel are heated on a water bath for three minutes, after which an additional 1 ml of sodium acetate is added and heating on the water bath continued for 15 minutes. To the cooled solution is added 3 ml of chloroform and the whole shaken for one minute; after the layers have separated the chloroform solution is poured off into a small beaker (50 ml). The extraction is repeated twice again, the extracts being collected in the same beaker. To this solution is added 10 ml of water and the chloroform evaporated off; 1 ml of HNO_3 (sp.gr. 1.4) or 2-3 drops of hydrogen peroxide and 0.5 ml of H_2SO_4 (sp.gr. 1.84) are then added, and the solution evaporated almost to dryness. To the residue is added 1 ml of 1 N HCl, 5-6 ml of water and the solution heated until it has dissolved completely; the aluminum is finally determined as described above.

Determination of Beryllium. The solution obtained after removal of the zirconium is heated in order to remove any residual chloroform; after cooling, depending on the volume, the solution is transferred to a 25-or 50-ml standard flask. An aliquot of this solution containing 0.5 to 5 μg of beryllium (1-5 ml) is transferred to

* 42 g of sodium acetate is dissolved in a 1000-ml standard flask, 11.8 ml of glacial acetic acid is added and the volume made up to the mark. 0.1 g of aluminon is dissolved in 100 ml of this solution.

** 5 g of hydroxyquinoline is dissolved in 100 ml of 2N CH_3COOH. 1 ml of such solution precipitates about 3 mg of Al.

a quartz beaker, 1-2 drops of H_2SO_4 (sp.gr. 1.84) added, followed by one drop of hydrogen peroxide, and the solution evaporated almost to dryness. The residue is dissolved on heating in water and the solution transferred to a 25-ml standard flask. To this solution is added 0.2 ml of a 5% solution of ascorbic acid (for reducing traces of iron), and 0.5 ml of a 5% solution of sodium ethylenediaminetetraacetate for complexing aluminum, magnesium, etc. (which are not extracted with zirconium as their cupferronates).

After alkali has been added until the pH is about 12, the beryllium is determined photometrically by means of beryllon [14].

TABLE 3

Determination of Al and Be in Zirconium

Taken			Found	
zirconium, mg	aluminum μg	beryllium, μg	aluminum, μg	beryllium, μg
100	60	—	63	—
100	60	2	58	1,9
100	40	5	41	4,9
100	300	50	300	50,5
50	—	2	—	1,9
20	20	2,5	19,5	2,6

The method is fairly sensitive and permits the determination of 5×10^{-4}% beryllium in zirconium (the error is about 4-5% relative).

Table 3 contains results of the determination of aluminum and beryllium in synthetic mixtures containing zirconium.

Determination of Uranium. Uranium is determined photometrically using hydrogen peroxide in a carbonate medium [15].

The determination is carried out on an aliquot of the solution remaining after removal of the zirconium, and treated in the same way as that described above for the determination of beryllium. The elements remaining in the solution after extraction of zirconium and other impurities do not interfere with this determination. Before extracting zirconium the uranium should be oxidized to the hexavalent state.

Determination of Magnesium. Magnesium is determined photometrically by means of titanium yellow, either directly after removal of zirconium if it is known that the solution is free from aluminum, or after removal of aluminum by extraction of the 8-hydroxyquinolate of the latter by chloroform, with the addition before extraction of excess (up to 50%) of a 5% acetic acid solution of 8-hydroxyquinoline.

To an aliquot of solution obtained after removal of zirconium and aluminum is added 2-3 drops of concentrated H_2SO_4, one drop of hydrogen peroxide, and the solution evaporated almost to dryness. The residue is dissolved on heating in water. The solution is transferred to a 50-ml standard flask, 1 ml of a 0.05% solution of titanium yellow is added; this is followed by 10 ml of 2 N alkali solution and the volume made up to the mark with water. The optical density is measured in a cuvette with a layer thickness of 50 mm, a green filter (λ about 530 mμ) being used.

The sensitivity of the method is 5×10^{-3}%. The accuracy of the method for hundredths of a percent is 5-7% (relative). Large amounts of beryllium interfere with the determination.

Determination of Zinc [16]. Zinc is determined, after removal of zirconium (and aluminum), by titration with sodium ethylenediaminetetraacetate in the presence of eriochrome black T (ET 00) as indicator. The method permits determination of 0.1% and more of zinc with an accuracy of 1-2% (relative). Magnesium should be absent.

SUMMARY

It is suggested that zirconium can be extracted from a 1 N sulfuric acid solution by means of chloroform solution of nitrosophenylhydroxylamine. It has been shown that two extractions ensure quantitative removal of zirconium into the chloroform, while aluminum, beryllium, magnesium and other elements remain completely in the aqueous solution.

The method can be used for the determination of aluminum, beryllium, uranium, magnesium, and zinc in zirconium and in alloys based on zirconium.

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* Original Russian pagination. See C.B. Translation.

POTENTIOMETRIC MICROTITRATION OF HALOGENS IN ORGANIC COMPOUNDS AFTER THEIR MINERALIZATION

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One of the most reliable methods of mineralizing organic materials is fusion with potassium metal in a bomb at 800-850° [1, 2]. Instead of determining the halogen ions by mercurimetric titration [1] after the compounds have been fused with potassium, we have applied successfully their separate potentiometric microtitration with a solution of a Ag salt. Current methods of argentometric potentiometric microtitration reduce mainly to the following techniques. Ingram [3] titrated chloride, bromide, and iodide ions with silver nitrate using two silver electrodes. Cogbill and Kirklan [4] also titrated halide ions with silver nitrate using silver electrodes, one of which was amalgamated. The method is not very practical since the amalgamated electrode has to be changed daily. Inglis [5] titrated halide ions with platinum and mercuric sulfate electrodes. Levy [6, 7] titrated halide ions separately and in their mixtures with silver nitrate using a silver and a calomel electrode; when this technique is used high results are obtained for bromide and low results for chloride as a result of coprecipitation of chloride with bromide; an empirical correction is therefore applied. The end point is determined from the titration curves or by titrating to the equivalent potential.

Varying amounts of potassium metal are taken for fusion; accordingly, the concentration of the salt in the solution being titrated varies, and titration to an equivalent potential is not possible. In the work described here the end point was determined on the basis of the maximum potential jump per unit volume of titrant added; the electrodes used were a silver electrode and a saturated calomel electrode. Titration was carried out in a volume of 15 ml (with a halide ion content of about 2-3 mg) in the presence of 0.5 N sulfuric acid; the titrant was 0.01 N silver nitrate. Near the end point the potential was read off 30 seconds after addition of each portion of titrant (0.02 ml). The maximum potential change (when the volume of the solution being titrated is 15 ml) for chloride ions was 10-15 mv, for bromide ions 50-70 mv, and for iodide ions 100-150 mv; chloride and bromide ions could be determined separately without any difficulty. Cyanide ions, which interfere with determination of chloride and bromide, were oxidized with hydrogen peroxide in an alkaline medium. Hydrogen sulfide was removed by heating the acidified solution. During determination of iodide, treatment of the test solution with hydrogen peroxide leads to loss of iodine. Since the potential jump for iodide ions occurs considerably earlier than that for cyanide ions, the presence of the latter has hardly any effect on titration of iodide ions, and the treatment with hydrogen peroxide can be omitted. The results obtained are given in Table 1.

As mentioned above, during titration of mixtures of the halide ions, as a result of coprecipitation of chloride with bromide ions, high results are obtained for bromide and low results for chloride. In order to diminish the coprecipitation of silver chloride with silver bromide, barium nitrate, ammonium nitrate, sodium nitrate, etc. have been added to the solution being titrated [8]. We used potassium nitrate. Titration of mixtures of chloride and bromide ions was carried out, in contrast to Levy [7], on one aliquot. During titration of mixtures of the halides the potential jump decreased: for chloride to 5-8 mv, and for bromide to 15-18 mv. Table 2 contains results of the determinations of chloride and bromide in synthetic mixtures.

TABLE 1

Separate Determination of Halide Ions

Organic compound	Theoretical content, %	Halide found, %	Deviation, %
Di-α-chloropropyl ketone	38,73	38,90 38,89	+0,17 +0,16
Dimethylchloromethyl-n-tertiary-butylphenylmethane	15,77	15,66 15,99	—0,11 +0,22
1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropylmethyldichlorosilane	25,96	26,11 25,95	+0,15 —0,01
ω, ω-Dibromoacetophenone	56,30	56,11 56,28	—0,19 —0,02
4-Bromotetrahydrofuranone-3	48,60	48,70 48,71	+0,10 +0,11
The hydrochloride of the nitrile of β-(1,2,5-trimethyl-4-phenyl-4-hydroxy-piperidyl-5)-propionic acid	11,58	11,38 11,65	—0,20 +0,07
A complex compound of 5,11,17-trioxo-8,14-dithiouneicosane with two molecules of mercuric chloride	16,09	16,28 15,92	+0,19 —0,17
Monoiodomethylate-3,4-bis (N-piperidinomethyl)-2,5-dimethylthiophene	28,37	28,30 28,31	—0,07 —0,06

TABLE 2

Simultaneous Determination of Chloride and Bromide in Synthetic Mixtures

Mixture	Sample wt., mg	Theoretical content, %	Halide found,%	Deviation, %
Dichloroanthracene	22,42	28,70	28,44	—0,26
Bromoindane	23,67	67,55	67,39	—0,16
Dichloroanthracene	28,71	28,70	29,10	+0,40
Bromoindane	12,11	67,55	67,51	—0,04
Hexachloroethane	21,42	89,85	89,90	+0,05
Bromobenzoic acid	22,40	39,75	40,06	+0,31
Chlorobenzoic acid	34,98	22,65	22,49	—0,16
Dibromoformylacrylic acid	28,93	61,98	62,41	+0,43

Experimental Procedure. The indicator electrode was a silver disc 3 × 5 mm, which was cleaned with emery cloth; it was rubbed with alcohol and then rinsed with water and left for some time in a solution containing bromide ions (the electrode for titrating chloride and bromide ions) or iodide ions (for iodide). The reference electrode was a saturated calomel electrode. The salt bridge was filled with a saturated solution of potassium nitrate. A P-4 potentiometer was used for measuring the emf. The 0.01 N silver nitrate solution was standardized against chemically pure sodium chloride. An aliquot of the organic material (15-25 mg) was fused with potassium metal in a bomb [1, 2]. The solution obtained was collected in a 100-ml standard flask and filtered. A 10-ml aliquot was transferred for titration into a 30-40-ml beaker; 10 drops of a 15% solution of hydrogen peroxide was added and the whole heated almost to the boiling point for 5-7 minutes in order to oxidize cyanide ions. For iodide determination, treatment of the sample with hydrogen peroxide was omitted. When the test material contained sulfur, the solution, after removal of cyanide ions, was acidified with 0.5 N sulfuric acid and again heated until there was no odor of hydrogen sulfide. The beaker walls were rinsed with a small amount of water (the total volume should not exceed 15 ml). After cooling, the solution was acidified with 0.5 N sulfuric acid using phenolphthalein as indicator, and 1 ml of acid in excess added. The electrodes were immersed in the solution and the latter titrated with 0.01 N silver nitrate using a magnetic stirrer. Initially, the titrant was added in large aliquots (1.0-0.5 ml each), the potential being read off each time. Near the end point (approximately 0.1 ml before the end) the solution was added in portions of 0.02 ml and the potential measured after 30 seconds. The end point was determined for the maximum change in potential. During titration of mixtures of chloride and bromide ions the aliquot was treated as described above. Three g of potassium nitrate was added to each test before titration. A pilot titration was carried out first so that in subsequent titrations it was possible to add almost all the silver nitrate at once. The potential was measured 30 seconds after each addition of titrant. Bromide ions were titrated first and then chloride ions. The accuracy of a separate determination is ± 0.3%, while the accuracy of a simultaneous determination is ± 0.5%.

SUMMARY

It has been shown that it is possible to determine iodide ions, and to carry out simultaneous and separate determinations of chloride and bromide ions, in the solution obtained by fusing halogen-containing compounds with potassium metal; potentiometric titration with a solution of $AgNO_3$ is used as a finish. The accuracy of the method is ± 0.3%.

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ANALYSIS OF FLUOROORGANIC COMPOUNDS.

SIMULTANEOUS MICRODETERMINATION OF FLUORINE, CARBON, AND HYDROGEN

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The present article contains a detailed description of a method for the simultaneous determination of fluorine, carbon, and hydrogen; the fundamental principles of this method have been outlined in previous papers [1-3]. This method has already been in use in our laboratory for three years, and its reliability has been confirmed by the analysis of several hundreds of fluoroorganic compounds. It is applicable to the analysis of solid, liquid, and gaseous materials containing oxygen, nitrogen, sulfur, chlorine, bromine, boron, silicon, and phosphorus in addition to carbon, hydrogen, and fluorine.

The Essentials of the Method. The test material is subjected to pyrolytic combustion in a quartz tube in a layer of magnesium oxide. In the course of this method C and H are determined as usual from the weight of CO_2 and H_2O formed, while fluorine remains in the magnesium oxide layer in the form of magnesium fluoride. The MgO containing the MgF_2 is then swept with steam at 1000°. At this stage all the fluorine is liberated in the form of HF, which is entrained in a receiver containing distilled water. Fluoride ions are finally determined by a thorimetric titration. Examples of the determination of C, H, and F in various materials are are given in the table.

Apparatus. The standard apparatus used for the determination of carbon and hydrogen is used after some modifications and additions. The combustion tube has an over-all length of 550 mm, an external diameter of 14 mm, and an internal diameter of 12 mm. The quartz tubes used for holding the samples are 90 mm long and have an external diameter of 8-8.5 mm and an internal diameter of 6-6.5 mm. Thick-walled quartz capillaries (Fig. 1) are used for aliquots of liquid test materials; these capillaries can be used repeatedly. Glass capillaries are not recommended, since during combustion the magnesium oxide is contaminated with lumps of glass and may interfere with subsequent pyrohydrolysis, and may spoil the apparatus. Tongs with soldered bent tips which closely grip the quartz tubes are suitable for handling tubes filled with calcined magnesium oxide. The following equipment is necessary: two MASN-11 ovens for heating the gas-purifying tube and the silver layer* in the combustion tube, when substances containing other halogens apart from fluorine are analyzed; one open oven MA-14 and one electric MAG-6R burner for burning the sample and for heating the magnesium oxide. The general appearance of the combustion tube is shown in Fig. 2.

The setup used for pyrohydrolysis (Fig. 3) consists of a steam generator, a steam superheater, a tube for pyrohydrolysis, a receiver, and an electric heating apparatus. A 0.5- to 1-liter flask with a wide neck serves as a steam generator. The flask is heated on an electric hot plate or on a flask heater connected to the source via a laboratory autotransformer. The steam superheater is made from clear quartz. The outlet tube is fitted with a ground cone for connecting with the pyrohydrolysis tube. The superheater is heated to 1000-1100° by means of a MA-02-20 oven. In order to cut down the loss of heat at the point where the steam issues from the superheater, the outlet tube is wound with asbestos cord. The tube used for pyrohydrolysis should be made from material

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*The silver can also be heated with the MAG-6R electric heater.

TABLE

Determination of Fluorine, Carbon, and Hydrogen on One Aliquot of Material

Test material	C, %		H, %		F, %	
	found	difference	found	difference	found	difference
Di-β-hydroperfluoroisobutyl ether of hydroquinone $C_{14}H_6F_{16}O_2$ Calc. C32,96 % H 1,19 %; F 59,59%	32,71 32,68	—0,25 —0,28	0,90 0,90	—0,29 —0,29	59,18 59,40	—0,41 —0,19
Perfluoroallylphenyl ether $C_9H_5F_5O$ Calc. C 48,23%;H 2,25%; F 42,39%	48,24 47,99	+0,01 —0,24	2,41 2,25	+0,16 0	42,22 42,15	—0,17 —0,24
α,β-Difluorobromoethylene $C_2Br_2F_4$ Calc. C 9,24%;F 29,25%; Br-61,51%	9,29 9,20	+0,05 —0,04	— —	— —	28,98 29,13	—0,27 —0,12
The amide of difluorochloroacetic acid $C_2H_2ClF_2NO$ Calc. C 18,54%; H 1,56%; F 29,35%; C 127,39%	18,26 18,49	—0,28 —0,05	1,42 1,48	—0,14 —0,08	29,57 29,53	+0,28 +0,18
The ethylamide of β-hydroperfluoroisobutyric acid $C_6H_7F_6NO$ Calc. C 32,30; H 3,16; F 51,09%	32,35 32,54	+0,05 +0,24	3,17 3,08	+0,01 —0,08	51,15 50,97	+0,06 —0,12
Piperidide of β-hydroperfluorovinyl acetic acid $C_9H_{11}F_4NO$ Calc. C 48,00%; H 4,92%; F 33,75%	47,86 48,16	—0,14 +0,16	4,87 4,89	—0,05 —0,03	33,58 34,00	—0,17 +0,25
The complex of boron fluoride and acetic acid $C_2H_4O_2 \cdot 20,5BF_3$ Calc. C 32,48%; H 5,45%; F 15,80%	32,32 32,35	—0,16 —0,13	5,58 5,60	+0,13 +0,15	15,71 15,53	—0,09 —0,27
β, β'-Difluorodiethyldimethylphosphinate $C_5H_{11}F_2O_3P$ Calc. C 31,92%; H 5,89%; F 20,20%	31,75 32,03	—0,17 +0,11	5,87 5,93	—0,02 +0,04	20,04 20,18	—0,16 —0,02
O,O-Diethyl-S-β-fluoroethylthiophosphate $C_6H_{14}FO_3PS$ Calc. C 33,35%; H 6,53%; F 8,79%	33,39 33,59	+0,04 +0,24	6,60 6,56	+0,07 +0,03	9,36 9,06	+0,57 +0,27

Note: All the analyses were carried out on aliquots of 4-9 mg.

which is stable for a long time to the action of HF mixed with steam at 1000-1100°. Apart from platinum, which is the best material for this purpose, we can also recommend soft nickel tube (type N-3, GOST 849[*]), which will stand up to more than 100 determinations, and, thanks to its cheapness and ready availability, can compete with platinum. The tube dimensions are as follows: length 400-425 mm, internal diameter 10-11 mm, wall thickness for nickel 1 mm and for platinum 0.5 mm. The part of the tube connected to the steam superheater is fitted with a ground joint (it has been shown that it is possible in practice to work without a ground joint, as long as the ground cone fits sufficiently tightly into the tube). From the side of the ground joint, at a distance of 1 cm from the end of the tube, the tube is wound for a length of 160 mm with IÉ-594 thermostable alloy (diameter of the wire 0.5 mm, approximate length 7 meters, number of turns 100-110). It is also possible to

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[*] We used tubing made up by the Revdinskii plant.

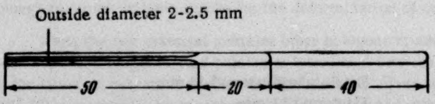

Fig. 1. Quartz capillary.

use a dismoutable electric oven type MA-02-20 at a temperature of 1150° (in this case the pyrohydrolysis tube should be 4 cm longer), but it is much more convenient to use the wire winding. At a distance of 2 cm from the oven to the nickel tube a brass condenser 12-14 cm long is fused on; when a platinum tube is used a quartz or brass coupling is fitted on by means of rubber tubing. The cold end of the tube sticking out of the condenser is 11-12 cm long. In order to keep the layer of magnesium oxide being pyrohydrolyzed in the hottest part of the tube, a diaphragm of platinum mesh folded in two is fitted into the tube by means of a rod, and the diaphragm fixed in such a position that the magnesium oxide is located in the center of the heated zone during pyrohydrolysis. A 100-ml flask with a wide neck is used as the receiver.

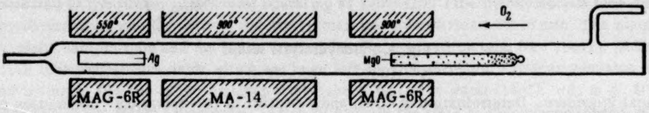

Fig. 2. Combustion tube.

The fluoride ions are titrated using a 10-ml microburet with scale divisions of 0.02 ml.

Preparation of Magnesium Oxide. Powdered magnesium oxide is mixed into a paste, placed in a Petri dish and dried at 110-120° prior to breaking up the surface; it is then ground in a porcelain mortar and sieved. Material which is retained on No. 1 and No. 2 sieves is used. A portion of the sieved preparation is placed in a layer 17-18 cm long in an aged combustion tube, and is calcined at 900° as for the determination of C and H in fluorides [4] by connecting the tube to a setup actually used for determination of C and H, or it is connected to a special setup. The drying time is 1.5 hours from the moment at which the oven is switched on. Such treatment of the magnesium oxide is accompanied by a decrease in volume of 1.5-2. The magnesium oxide is then strewn into a flask fitted with a rubber stopper, in which it is stored until it is finally conditioned in the pyrohydrolysis tube. Immediately prior to its use for an analysis the requisite amount of MgO, measured out in one of the tubes used for holding samples, is strewn into the pyrohydrolysis tube, heated beforehand to 1000-1100°; steam is passed through for 5-10 minutes a further half-tube-full of MgO is then added and the whole pyrohydrolyzed for a further 30 minutes. Dense granules which do not tend to form dust are obtained; these are strewn into a quartz tube sample holder and this is placed in the combustion tube in which it is heated at 900° for 20 minutes in a MA-14 oven, oxygen being passed through at the rate of 30 ml/minute. A second portion of magnesium oxide is prepared in exactly the same way, and, during the analyses, first one and then the other portion is used in turn. In order to get correct values for fluorine with a new preparation of magnesium oxide, it is necessary to carry out four to five combustions of pure fluoride, the preparation being pyrohydrolyzed after each combustion [3] (for C and H correct results are obtained starting from the first combustion); determination of F, C, and H is not obligatory in these cases.

Preparation of Buffer Solution [5]. 100 ml of accurately prepared 1 N monochloroacetic acid is measured out and is neutralized with 1 N alkali using phenolphthalein as indicator. A further 100 ml of monochloroacetic acid is added and the volume made up to 500 ml. The solution thus prepared should have a pH of 2.9-3.0 (check by potentiometer).

Preparation of Thorium Nitrate Solution. 0.025 N thorium nitrate solution is prepared by dissolving 3.45 g of dry $Th(NO_3)_4 \cdot 4H_2O$ in one liter of water. The solution is standardized by weighing the calcined dry residue.

When the pyrohydrolysis is carried out in a nickel tube rather than a platinum tube, some of the fluorine may be lost in the apparatus. According to our observations this loss is proportional to the fluorine content of the sample. In such cases it is recommended that the titer be established on the basis of the results of combustion of two to three aliquots of pure material.

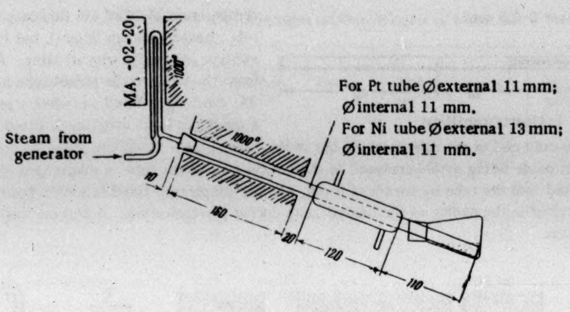

Fig. 3. Pyrohydrolysis setup.

Analytical Procedure. Determination of C, H, and F consists of two operations—combustion of an aliquot and pyrohydrolysis of magnesium fluoride. For the sake of clarity we shall describe these operations in sequence, although in actual practice the analyst simultaneously carries out combustion of the aliquot and pyrohydrolysis of the magnesium oxide from the preceding combustion.

Determination of Carbon and Hydrogen. A blank run is carried out at the beginning of the working day. While the absorption apparatus is being weighed, a quartz tube 9 cm long containing only just-pyrohydrolyzed MgO is inserted into the combustion tube and is moved into that part of the tube which is heated to 900° by the MA-14 oven. The tube containing MgO is calcined for 20 minutes. The weighed absorbers are connected to the combustion tube, and, while the aspirator tap is closed, the tube containing MgO is moved out of the oven into the cold part of the tube for 10 minutes. During this period an aliquot of test material (4-8 mg) is measured out into a clean quartz sample tube and strewn with magnesium oxide which has been cooled in the cold part. The quartz sample tube is then placed in the combustion tube, the aspirator tap is opened, and combustion is started. Aliquots of high-boiling nonvolatile liquids are placed in thick-walled quartz capillaries (see Fig. 1.), which are placed in the quartz sample tube with their open ends toward the bottom, and are then strewn with magnesium oxide as in the case of solid test material. Combustion of the sample is carried out with an electric heater operating at 900°, or with a gas burner: Oxygen is passed through at the rate of 35 ml/minute. At the beginning of combustion the electric burner should cover 3-4 cm of the tube (the sample holder) from its open end. The electric heater and, behind it, the MA-14 oven are shifted forward toward the closed end of the tube, the combustion rate being readily controlled bv observing formation of carbon on the magnesium oxide. Combustion is complete after 10-15 minutes. The tube containing the magnesium oxide is left in the heated zone for 5-7 minutes for decomposition of the magnesium carbonate which is formed. The electric heater is then completely removed, the long oven taken away, and the abosrption apparatus separated from the setup and weighed as usual. The tube in which the fluorine has been absorbed by magnesium oxide is removed from the combustion tube and transferred to the pyrohydrolytic setup. Another portion of magnesium oxide which has just been pyrohydrolyzed is strewn into a quartz sample tube and is inserted into the combustion tube as described earlier. During all the operations with magnesium oxide it is necessary to remember that it should only be allowed to come into contact with the air during the period that is required for strewing it from one quartz sample tube to another, i.e., only a matter of seconds. The speed with which magnesium oxide is handled determines to a considerable extent the value and reproducibility of the corrections which have to be applied for the CO_2 and H_2O which it absorbs from the air. Magnesium oxide which is to be used for combustion or for calcining prior to combustion should not be left to stand in the air.

The operation of the setup is checked by carrying out a combustion of a pure fluorine-containing material, and introducing the appropriate corrections for the weight of CO_2 and H_2O. The value of these corrections depends mainly on the temperature conditions used for conditioning the magnesium oxide, and also on the time for which the conditioned magnesium oxide comes into contact with the air when it is being transferred from one quartz tube sample holder to the other; the correction factor is 175-200 μg for water and 100-150 μg for carbon dioxide. Despite the large value of these corrections they are readily reproducible and are constant enough to ensure reliable results for the determination of carbon and hydrogen.

When the test material contains other halogens in addition to fluorine, metallic silver or silver which has been deposited on granulated pumice is introduced into the end of the combustion tube; a layer of 5-8 cm long of the silver on pumice is used, while the metallic silver and the silver on pumice is heated to 575° or up to 425° [6] respectively by an electric heater or by a MA-SN-11 electric oven. When the test material contains chlorine or bromine, platinum contacts cannot be placed in the oxidizing zone [3].

During the analysis of materials containing sulfur, phosphorus, silicon, and boron the quartz sample tube containing magnesium oxide is placed in an empty combustion tube.

Fluorine Determination. At the beginning of the analysis the electric heater of the pyrohydrolysis tube, the steam superheating oven, and the flask heater are all switched on. When the water in the steam generator is boiling, and the necessary steam throughput (0.5 ml/minute of condensate) has been attained, the pyrohydrolysis tube is connected to the stream superheater operating at 1000-1100° (the pyrohydrolysis tube contains magnesium oxide pyrohydrolyzed the day before); the MgO is then treated with steam for 15 min. The magnesium oxide is strewn into a quartz sample tube and the latter is placed in the combustion tube (see above), while into the free pyrohydrolysis tube magnesium oxide which has been left unpyrohydrolyzed after combustion carried out the previous day is strewn; the end of the pyrohydrolysis tube is placed in water (10-15 ml) in a 100-ml conical flask and is connected to the steam superheater. After 20 minutes the flask is lowered so that the end of the tube does not touch the liquid; the outside of the tube is washed and after a further 10 minutes the receiver is withdrawn. The pyrohydrolysis tube is swept with steam up to the beginning of the next determination. The hydrolyzate is transferred to a 100-ml standard flask and its volume made up to the mark with distilled water; three aliquots of 25 ml are transferred to 100-ml conical flasks. To each flask is added 0.4 ml of a 0.1% solution of sodium alizarine sulfonate and the solution neutralized with 0.02 N NaOH to the appearance of a violet color: It is finally titrated thorimetrically [5].

The limiting concentration which can be determined is about 1 mg of fluorine in an aliquot of solution; this corresponds to the use of 2 ml of thorium nitrate solution. At higher fluorine concentrations the solution acquires a red color prior to the equivalence point and low results are obtained. Accordingly when fluorine-containing compounds with a high fluorine content are being analyzed, it is recommended that the hydrolyzate be diluted to 250 ml.

1 ml of 0.025 N thorium nitrate solution corresponds to 0.475 mg F.

An analyst can carry out four determinations in the course of a six-hour working day.

SUMMARY

A method is described for the simultaneous microdetermination of fluorine, carbon, and hydrogen in solid and liquid organic materials containing various elements.

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DETERMINATION OF PHENOLIC HYDROXYLS IN TECHNICAL LIGNINS BY A POTENTIOMETRIC METHOD

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Phenolic hydroxyls are characteristic functional groups of the lignin complex, and their accurate quantitative determination in various lignins is very important. Current methods of determining these groups are not sufficiently accurate when they are applied to the various forms of technical lignins; most of them only give positive results in the case of soluble samples. One of the first chemical methods [1] was based on methylation of the phenolic hydroxyls with diazomethane, with subsequent determination of methoxy groups. Subsequently, the authors themselves acknowledged that this was not accurate enough. Recently a new technique (the so-called periodate method) has been suggested [2]. Sodium periodate oxidizes methoxy groups to methanol only in the presence in the molecule of free phenolic hydroxyls located in the ortho position, the amount of methanol formed being approximately equal to the amount of phenolic hydroxyls. The periodate method gives satisfactory results for isolated lignins such as those of Brauns and Bjorkman, but is not suitable for technical polymerized lignins which include decomposition products and polysaccharide residues.

Other chemical methods are also known—bromination, azo-coupling, etc.

Freudenberg [3] and Enquist [4] have titrated phenolic groups potentiometrically according to a method suggested by Brockman and Meyer [5]. Samples are titrated in ethylenediamine, pyridine, or dimethylformamide with sodium colamine. Unsatisfactory results were obtained, however, for a whole series of model materials. Enquist et al. [4] suggested determination of the amount of phenolic hydroxyls for ligno-thioglycolic acid and ligno-sulfonic acids as the difference between the total acid groups and strongly acid groups, by separate titration in an organic solvent and in water (or in an aqueous solution of alcohol). Fritz et al. [6] have developed a method for the determination of phenolic groups by titrating with potassium methylate in dimethylformamide. These authors have found that the presence in the ortho- or para-position of aldehyde, ketonic, ester, or ether groups, and alkyl radicals increases the acid strength of the phenolic hydroxyls. Carboxyl groups do not exhibit such an effect. Butler and Czepiel [7] who studied the latter method, carried out a potentiometric titration with antimony and saturated calomel electrodes. They analyzed a series of model materials and samples of lignin which are soluble in dimethylformamide, and obtained results which were in good agreement with those of other methods.

Sarkanen and Schuerch [8] carried out a conductometric titration of phenolic hydroxyls in isolated lignins by Kolthoff's method. The solvent used was ethanol and acetone to which water had been added, while the titrant was an aqueous solution of lithium hydroxide. Under these conditions, good results were obtained for ethanol-lignin, "natural" Brauns lignin, and alkaline lignins. The weak phenolic hydroxyls of technical lignins were, however, not nitrated by this method.

Syskov and Kukharenko [9] have suggested a sorption method for the determination of insoluble lignins. The analysis is based on the phenomenon of adsorption of an aqueous solution of barium hydroxide and the chemical interaction of the latter with the acid groups of the lignins. This method was modified by Ekman [4], who heated the reaction mixture to 85°. Heating accelerates the chemical reaction and leads to a decrease in physical adsorption, which is the reason for the usual high amounts of acid groups. However, during the analysis of technical hydrolyzed lignins and products of their alkaline activation ("ligno-acids") in our laboratory, high and variable results were obtained.

Aulin-Erdtman [10] and Goldschmidt [11] carried out a spectrophotometric determination of the amount of phenolic groups, which consists of measuring the shift in the ultraviolet in neutral and alkaline media. The optical method has not always proved to be accurate for model materials, and gave low results comparable to those obtained by the potentiometric method; this can be explained in certain instances by steric hindrance (particularly, for diphenyl derivatives). The latter method can only be used for lignins which are soluble in water or organic solvents (ethanol, dioxane).

We wanted to determine the phenolic hydroxyl content of insoluble lignins, such as technical sulfate and hydrochloride lignins, and of products of their chemical activation. The method described by Butler and Czepiel [7] was modified, and 11 samples of lignin and three model materials were potentiometrically titrated in dimethylformamide with potassium methylate.

Since the phenolic hydroxyls of lignins are very weak acids, titration must be carried out in an absolutely anhydrous medium in order to produce a sharp potential jump near the equivalence point [12]. Almost all the samples of lignins which we tested were sparingly soluble in dimethylformamide. Attempts to use Butler's method as it stood gave unsatisfactory results; agreement could not be obtained between results in parallel determinations. Acting on the assumption of the existence of reactive groups in lignin (including phenolic groups) on the surface of the macromolecule [13], we adopted the method of boiling the test preparations in dimethylformamide for ensuring maximum development of this surface and converting the insoluble lignin into a weighable state while it is highly dispersed. The possibility of titrating a suspension of lignin (after boiling in dimethylformamide) is in agreement with the work of Oden [14], who successfully potentiometrically titrated a suspension of humic acids for determination of their equivalent weight. After many attempts, we succeeded in developing a technique which gave consistent results in parallel determinations, and which were in good agreement with the results of other research workers.

EXPERIMENTAL

Preparation of Reagents. a) Solution of Potassium Methylate in Benzene. Absolute methanol dried over calcined calcium oxide, and dry benzene distilled over potassium metal were used for preparing the solution.

20 ml of methanol and 50 ml of benzene were mixed in a one-liter flask, 2 g of freshly cut potassium metal was then added in small lumps. When the turbulent reaction had ceased, another 55 ml more of methanol was added and the mixture made up to one liter with benzene. The potassium methylate solution was standardized against benzoic acid.

b). Dimethylformamide was distilled and the fraction boiling between 152-153.5° was chosen.

Preparation of Lignin Samples. The samples, which were washed with water until they gave a neutral reaction, were then dried and given a preliminary extraction with ether. They were then dried again to constant weight, first over silica gel in a vacuum, and then over P_2O_5 in a vacuum at room temperature.

"Lignin acids" were prepared by a three-fold precipitation of lignin with sulfuric acid from its alkali solutions, obtained during activation of lignin sulfate by sodium hydroxide or CaO at 180°.

Biochemical lignin was prepared by methanolic extraction of defective wood which had been attacked by Poria vaporaria and Merulius lacrymans [15].

Saponified chlorolignin was prepared by cooking the latter (the chlorolignin was prepared by Shorygin's method [16]) in an autoclave with milk of lime containing 13 g of calcium oxide in 1 liter, at 180° for four hours: A stirrer was used.

Lignins were obtained from fir (Picea), pine, fir (Abies) and birch sawdust by treating the sawdust with a 40% solution of zinc chloride in 37% hydrochloric acid [17].

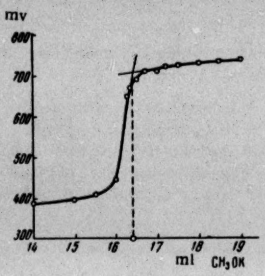

Fig. 1. Titration of benzoic acid with potassium methylate.

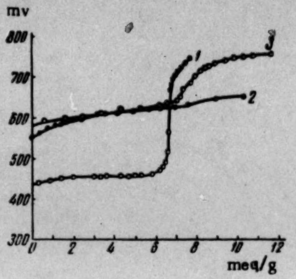

Fig. 2. Titration of model materials 1) Vanillin; 2) resorcinol; 3) guaiacol.

TABLE 1

Test material	Theoretical content		Found		Relative error
	meq/g	%	meq/g	%	
Vanillin	6,57	11,17	6,76	11,50	+2,85
Resorcinol	—	—	—	—	Not titrated
Guaiacol	8,06	13,69	8,15	13,86	+1,16

TABLE 2

Sample	OCH_3, %	Phenolic OH groups	
		meq/g	%
Biochemical lignin	12,79	3,13	5,28
Freundenberg lignin	15,80	1,80	3,06
Saponified chlorolignin	1,74	5,00	8,50
Lignin prepared according to the Popov method			
a) Fir (Picea)	—	1,75	2,98
b) Pine	—	1,65	2,81
c) Fir (Abies)	—	1,75	2,98
d) Birch	—	1,60	2,70
"Lignoacids" (hydrolyzed lignin, activated by NaOH)	10,81	3,0	5,10
"Lignoacids" (calcinified lignin, activated with CaO)	11,18	2,475	4,20
Hydrolyzed lignin sulfate	9,91	1,81	3,08
Lignin chloride	10,38	2,51	3,66

The titration setup consisted of a PLS-2 potentiometer constructed by VNIIGS, an electrolytic cell into which an antimony and a saturated calomel electrode were lowered (the electrodes being fixed in a stopper), a magnetic stirrer (KZMO), and a buret. Since the solvent removes the grease from the taps, a buret was used which was connected through a capillary tube to a rubber bulb fitted into a container fitted with a movable screw. By rotating the screw, solution could be let out of or sucked into the buret.

Titration Procedure. A blank test was carried out first. 15 ml of dimethylformamide was introduced into the electrolytic cell and acid impuriteis titrated potentiometrically. The potassium methylate solution was then standardized.

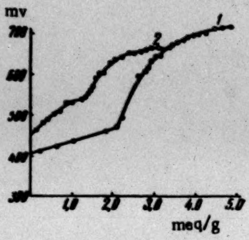

Fig. 3. Titration of lignin preparations. 1) Biochemical lignin; 2) Freudenberg lignin.

An aliquot of about 0.05 g of benzoic acid was dissolved in 15 ml of dimethylformamide and titrated with potassium methylate. When the titration had been finished a potentiometric titration curve was constructed (Fig. 1), from which the number of ml of CH_3OK used for titrating the benzoic acid and the acid impurities in dimethylformamide was determined .

The molarity of the potassium methylate was calculated by means of the formula

$$M = \frac{a \cdot 1000}{122\,(A - b)},$$

where a is the amount of benzoic acid taken; 122 is the molecular weight of benzoic acid; A is the number of ml of CH_3OK used for titrating the acid materials; b is the number of ml used in the blank test.

0.11-0.05 g of sample was taken, depending on the expected content of phenolic hydroxyls. Samples which were soluble in dimethylformamide were dissolved in 15 ml of the latter and titrated immediately. Lignins which were insoluble in dimethylformamide were given a preliminary boil for 60-120 minutes. After such a treatment the phenolic hydroxylsbecome more amenable to titration with potassium methylate. For this purpose an accurately weighed amount of lignin (about 0.1 g) was covered with 5 ml of dimethylformamide and the mixture boiled in a flask fitted with a reflux condenser. The condenser was sealed with a calcium chloride tube during the boiling process and during cooling. The solution was finally transferred quantitatively to the electrolytic cell and the flask rinsed out with 10 ml of dimethylformamide.

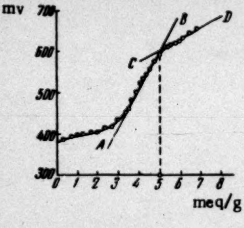

Fig. 4. Titration of saponified chlorolignin.

Titration was carried out by the usual method. Near the equivalence point the alkaline solution was added in lots of 0.2-0.5 ml. The potential was measured after the equilibrium value had been established (but not too slowly) the magnetic stirrer being switched off every time so as to exclude the effect of its magnetic field. The potential jump usually occurred at 550-650 mv. Titration was considered complete when the potential remained almost constant on addition of a further 6-7 drops. After completion of the titration, calculations were carried out and a titration curve constructed. The potentiometer readings in mv were plotted along the ordinate, and the milligram equivalents of CH_3OK per g of material calculated for each point, taking into account the reading in the blank test plotted along the abscissa. The end point was determined graphically [18] as the point of intersection of two lines. Corrections for the blank and determination of the concentration of the CH_3OK must be carried out periodically.

DISCUSSION OF RESULTS

Vanillin, resorcinol, and guaiacol were titrated as model materials. Good results which are comparable with the theoretical values were obtained for vanillin and guaiacol (Fig. 2). Resorcinol, which is a simple phenol, did not titrate. In alkaline solutions resorcinol, like pyrogallol and pyrocatechol, is vigorously oxidized by

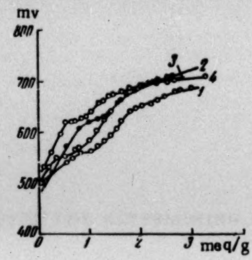

Fig. 5. Titration of lignins prepared by I.D. Popov's method. 1) Fir (Picea); 2) pine; 3) fir (Abies); 4) birch.

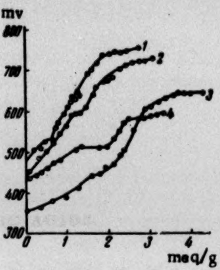

Fig. 6. Titration of technical lignins. 1) Hydrolyzed lignin sulfate; 2) hydrolyzed lignin chloride 3) ligno acids from alkaline lignin; 4) ligno acids from calcined lignin.

atmospheric oxygen and its solution darkened rapidly in the electrolytic cell during titration.

In Table 1 and Fig. 2 are shown the results and titration curves for the model materials.

In Figs. 3-6 are given titration curves for technical lignins and for some of its other forms; Table 2 contains the results for the phenolic hydroxyl content of the test materials.

SUMMARY

A potentiometric method for titrating the phenolic groups in lignin in dimethylformamide, following a preliminary boiling of the lignin in the same solvent, gives satisfactory results for insoluble lignin preparations, including technically hydrolyzed lignins.

The phenolic hydroxyl content of 11 lignin preparations is given.

It has been shown that it is possible to apply this method for determining the content of phenolic hydroxyls in aromatic products having an aldehyde or an ether group in the ortho-or para-positions (relative to the phenolic hydroxyl).

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A METHOD FOR DETERMINING BENZENECARBOXYLIC ACIDS

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In order to determine the number and position of substituents in the benzene ring in fractions of monocyclic aromatic hydrocarbons isolated by chromatography on silica gel from high-molecular-weight fractions of petroleum [1], we used the usual method of oxidizing with potassium permanganate in an alkaline medium (at a temperature of 98° [2]) and separating the mixture of carboxylic acids obtained by the method of Khodzhaev and Ibragimov [3]. The method consists of successive extraction of mono-, di-, and trisubstituted benzene carboxylic acids from a dry mixture of acids and potassium chloride by means of various solvents and using a special apparatus. The most vulnerable stage in the method is the determination of trimesic acid $C_6H_3(COOH)_3$, which is extracted by water together with the KCl, and is converted into its neutral barium salt $[C_6H_3(COO)_3]_2 \cdot Ba_3 \cdot 2H_2O$, which is insoluble in water, in order to determine it quantitatively.

Analysis of the barium salt obtained from pure, recrystallized trimesic acid gave results in agreement with theory (47.7% barium), while in samples obtained during the oxidation of a synthetic mixture of monocyclic aromatic hydrocarbons, or during oxidation of the appropriate fractions isolated from petroleum, the amount of barium in the precipitated trimesic salt amounted to 59%, which led us to assume the presenc of barium salts of other acids as impurities.

In order to establish the composition of the barium salts obtained, trimesic was re-formed from them by decomposing the salts with hydrochloric acid [4]. The analyses carried out showed that only small amounts of trimesic acid could be isolated from samples with a higher barium content than the theoretical value, while the barium salts prepared from pure trimesic acid gave results close to theory when trimesic acid was re-formed from them. On the assumption that oxalic acid was present we carried out a number of quantitative analyses using a standard method for determining oxalic acid [5]. It was found that during the oxidation of fractions of monocyclic aromatic hydrocarbons, followed by separation of the acids formed by the method of Khodzhaev and Ibragimov, oxalic acid accompanies trimesic acid; accordingly, determination of the latter as its barium salt cannot be carried out without an additional analysis for oxalic acid, which also gives a water-insoluble barium salt.

In addition to its titrimetric determination, oxalic acid can be separated from its mixtures with trimesic acid by means of distillation. The results of both these methods of determination showed reasonably close agreement.

In the experiments which we carried out on the oxidation of individual aromatic hydrocarbons (ethylbenzene, xylene, pseudocumene, mesitylene) oxalic acid was invariably present in the benzene carboxylic acids obtained. It should accordingly be present in all the acid fractions extracted by acetone in Khodzhaev and Ibragimov's method. The method described by these authors, although they used it for the quantitative separation of benzene carboxylic acids obtained during the oxidation of fractions of aromatic hydrocarbons from petroleum [6], was developed on the basis of synthetic mixtures of pure benzene carboxylic acids [3]; accordingly, they did not take into account the presence of oxalic acid.

SUMMARY

It has been shown that the benzene carboxylic acids which are formed during the oxidation of aromatic hydrocarbons from petroleum contain oxalic acid; the latter interferes in the method developed by Khodzhaev and Ibragimov.

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DETERMINATION OF SMALL AMOUNTS OF THIOUREA IN COPPER ELECTROLYTES USING A ROTATING PLATINUM ANODE

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The few known chemical methods [1-6] for the determination of thiourea in aqueous solutions are only applicable at comparatively high concentrations ($> 1.0 \times 10^{-3}$M), and even then are characterized by nonselectivity and by low accuracy.

Liberty [7], Edsberg [8], and Nyman [9] have studied the formation mechanism of the complex compounds of mercury and thiourea on a dropping mercury anode. In their work the polarograms did not have a clearly defined limiting current, and the latter changed appreciably with a number of factors.

Liberty and Gervone [10] have developed a method for the iodometric, amperometric titration of thiourea on a stationary platinum electrode. The authors only obtained reproducible results in a narrow thiourea concentration range (1.0×10^{-3} - 1×10^{-4}M) in neutral or weakly acid solutions, when other components were absent.

The potentiometric method suggested by Antropov [11] for the analysis of thiourea in copper electrolytes proved unsuitable for concentrations below $1.0 \cdot 10^{-3}$ M.

The present article contains the results of our studies and a method for the direct polarographic determination of microamounts of thiourea in copper electrolytes, using a rotating platinum anode.

Earlier [12, 14], the possibility had been demonstrated of using such electrodes for the determination of microamounts of organic materials subjected to an irreversible electrochemical oxidation.

The potential of the platinum electrode and the extent of its stability with time depend on the prehistory of the electrode and on the composition of the supporting electrolyte. The electrochemical treatment of the electrode according to a technique which we have used before [13-14] proved to be a necessary condition for obtaining reproducible current–voltage curves for the supporting electrolyte and thiourea.

The facts noted, and also the possible effect of dissolved oxygen (in an open cell) on the residual, and in particular on the initial current of the oxidation of thiourea, determined the necessity of studying the behavior of the platinum anode in the following solutions–supporting electrolytes: 1) 1 N H_2SO_4; 2) 1 N H_2SO_4 + 250 g/liter $CuSO_4 \cdot 5H_2O$; 3) 1 N H_2SO_4 + 250 g/liter $CuSO_4 \cdot 5H_2O$ + 0.5 g/liter of sodium naphthalenedisulfonate.

In Fig. 1 are given anodic polarograms of the supporting electrolytes taken on a rotating platinum anode in solutions of 1 N H_2SO_4 and 1 N H_2SO_4 + 250 g/liter $CuSO_4 \cdot 5H_2O$, the potential being applied at a constant rate of 4.9 mv/sec, by the "forward" and "reverse" method, i.e., at a rate "corresponding" to a linear increase and decrease of the applied positive potential within the limits 0.1-1.5 volt.

Immediately before each polarogram was taken the potential of the dead electrode was measured; These values are given in Fig. 1. A sufficiently negative potential was achieved by short-circuiting the test platinum and calomel electrodes for 2-3 minutes after taking each polarogram in turn.

It is clear from Fig. 1 (1 and 2) that reduction of oxygen on the platinum electrode occurs in the potential

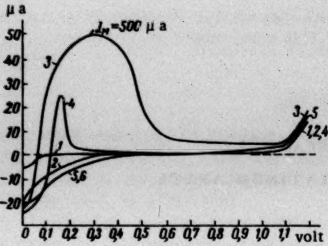

Fig. 1. Current–voltage curves for the supporting electrolytes, on a rotating platinum anode. Rate at which potential was applied 4.9 mv/sec. 1) Supporting electrolyte of 1 N H_2SO_4; $E_{initial}$ = = + 0.20 volt; 2) supporting electrolyte 1 N H_2SO_4; $E_{initial}$ = 0.50 volt; 3) supporting electrolyte 1 N H_2SO_4 + 250 g/liter $CuSO_4 \cdot 5H_2O$; $E_{initial}$ + 0.5 volt; 4) supporting electrolyte 1 N H_2SO_4 + 250 g/liter $CuSO_4 \cdot 5H_2O$; $E_{initial}$ = + 0.500 volt; 5) reverse polarogram, supporting electrolyte 1 N H_2SO_4 + 250 g/liter $CuSO_4 \cdot 5H_2O$; $E_{initial}$ = + 0.5 volt; 6) reverse polarogram; supporting electrolyte 1 N H_2SO_4; $E_{initial}$ = + 0.50 volt.

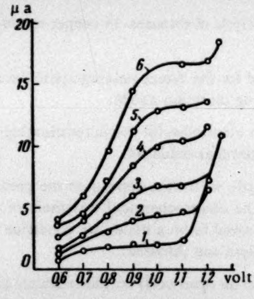

Fig. 2. Current–voltage curves for thiourea in a copper electrolyte, on a rotating platinum anode, rate at which potential was applied 4.9 mv/sec; R_{cell} = 200 ohms. 1) Supporting electrolyte 1 N H_2SO_4 + 250 g/liter $CuSO_4 \cdot 5H_2O$ + + 0.5 g/liter naphthalenedisulfonic acid; 2) thiourea $2.0 \cdot 10^{-5}$M; 3) $4.0 \cdot 10^{-5}$M; 4) $6.0 \cdot 10^{-5}$ M; 6) $1.0 \cdot 10^{-4}$M.

range up to + 0.5 volt. Under these conditions, the less positive the original potential of the electrode in the sulfuric acid medium, the smaller the influence of the reduction of oxygen on the initial residual current.

It was established that this is connected with the fact that in the same period of time, a comparatively large amount of dissolved oxygen succeeds in being reduced at the less positive potential. Thus, after a dead electrode with a potential of 0.2 volt has been standing for 10-15 minutes in a solution of 1N H_2SO_4, a considerable part of the dissolved oxygen (1) is reduced.

In anodic polarograms taken in a sulfuric acid medium (3,4), in contrast to polarograms taken in a weakly acid medium (1,2), there is observed a sharply defined maximum in the potential range 0.1 tot 0.3 volt. The value of the maximum current and of the residual current on the current–voltage curves for a copper electrolyte depends on the initial potential of the electrode: the more negative the initial true potential, the higher the maximum and the residual current.

It is evident that on the "reverse" polarogram (5) the maximum is absent, while its path coincides with the "reverse" polarogram for a solution of 1 N H_2SO_4 (6).

Similar current–voltage curves (which are shown in Fig. 1) were obtained in solutions–supporting electrolytes, containing sodium naphthalenedisulfonate in amounts of 0.5-1 g/liter. This leads one to conclude that under the conditions chosen for taking the polarograms, the naphthalenedisulfonic acid does not interfere with the diffusion limitations on the platinum electrode and, accordingly, should not interfere with the anodic polarographic determination of thiourea. The specific character observed for the anodic current–voltage curve for the supporting electrolyte (copper electrolyte) can be explained by the fact that in the potential range 0.08-0.50 volt on the platinum electrode two processes occur in parallel; reduction of oxygen and oxidation of copper ($\overset{0}{Cu} \rightarrow Cu^{2+}$).

Contact reduction of curpric ions on the platinum anode precedes the latter process, when the potential of the anode is more negative than + 0.2 volt; the "peak" which arises in the initial part of the polarogram of the supporting electrolyte has a phase characterized the moment at which the contact-precipitated coppper is expelled from the platinum surface.

That oxidation of copper does occur is additionally confirmed by the change in color of the anode (from the color of metallic copper to the color of platinum) during the process of taking current–voltage curves; and also by the fact that a dead platinum electrode after standing for 10-15 minutes in a copper electrolyte is covered by a thin film of copper, and acquires thereby a stable potential of 0.080 volt.

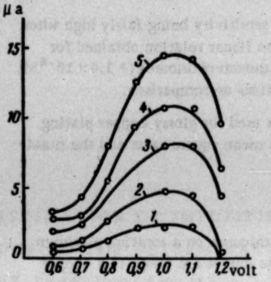

Fig. 3. Polarograms (after subtracting the residual current) for 2.0×10^{-5} to 1.0×10^{-4}M solutions of thiourea in a copper electrolyte on a rotating platinum electrode. Rate at which potential was applied 4.9 mv/sec: R_{cell} 200 ohms. 1) thiourea 2×10^{-5}M; 2) 4×10^{-5}; 3) 6×10^{-5}; 4) 8×10^{-5}M; 5) 1.0×10^{-4}M.

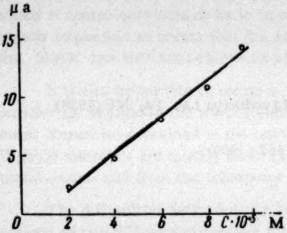

Fig. 4. Relation between the maximum current on the rotating platinum anode and the thiourea concentration in a copper electrolyte (for the series of experiments in Fig.3).

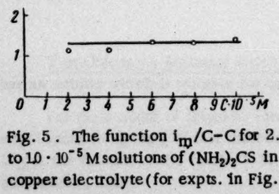

Fig. 5. The function $i_m/C-C$ for 2.0- to $1.0 \cdot 10^{-5}$ M solutions of $(NH_2)_2CS$ in a copper electrolyte (for expts. in Fig. 3).

The experimental results considered allow one to conclude that the use of a copper electrolyte as a supporting electrolyte for the polarographic determination of organic materials which are oxidized at high positive potentials (in particular, thiourea) is only possible under conditions which ensure reproducible preparation of the electrode, and when the polarograms are taken at potentials greater than 0.5 volt, when interference on the part of dissolved oxygen and copper ions is excluded.

The technique for the determination of thiourea in copper electrolytes consists of the following:

1) The rotating platinum anode is subjected several times (not less than three times) to anodic polarization (in the "forward" and "reverse" directions) in a solution of the supporting electrolyte in the range 0.6-1.3 volt.

Such an electrochemical treatment ensures, on the one hand, a strongly developed surface and consequently a high reaction capacity of the oxide-platinum electrode, and, on the other hand, a sufficiently high stability of the positive potential of the dead anode, which is shown by the slow drop in potential after taking the polarograms in turn.

2) The current–voltage curves are taken automatically at a constant rate (from 3 to 10 mv/sec), the potential difference being applied linearly, and the "zonal" method employed. The latter consists of switching the electric cell on and off at 0.6 and 1.3 volt respectively.

In Fig. 2 are shown a typical series of current–voltage curves which were produced for 2.0×10^{-5} - 1.0×10^{-4}M solutions of thiourea in a copper electrolyte. In this series of experiments all the curves were taken when the rate of application of the potential was 4.9 mv/sec, while the resistance of the cell was 200 ohms, and the temperature of the solution was constant.

The same polarograms are shown in Figs. 3, 4, and 5 (after subtraction of the residual currents), while the relation between the maximum current and the concentration, and function i_m/C - C, is also given. It is clear from Figs. 2-5 that the oxidation wave of thiourea extends over a wide potential range, a maximum being formed at a potential of 1.0-1.05 volt; the relation between the maximum current and concentration is linear, while the ratio i_m/C hardly changes at all with concentration. It has been established that the maximum currents on a rotating electrode are considerably greater than the maximum currents on a stationary electrode, and uniformly increase with increasing rotational rate of the electrode (up to about 1300 rpm). A large hysteresis loop was observed when both the "forward" and "reverse" current–voltage curves were taken.

It follows from this that the oxidation of thiourea in a copper electrolyte, as in a sulfuric acid medium [14], is controlled, in the main, by diffusion kinetics and proceeds irreversibly. The characteristics of the interaction of copper ions and thiourea in a copper electrolyte and the possible mechanism of the oxidation of thiourea on a platinum electrode are considered in another paper [14].

The method developed gives clearly defined and reproducible waves, the sensitivity being fairly high when determinations are based on the diffusion current. An essential feature is that the linear relation obtained for i_m/C makes it possible to carry out direct quantitative determinations of small amounts of thiourea ($> 1.0 \times 10^{-5}$M) in copper electrolytes comparatively rapidly and simply by the methods of additions or comparison.

Control measurements carried out by this technique on copper electrolytes used for glossy copper plating showed that for thiourea contents within the limits $1.0 \times 10^{-5} - 1.0 \times 10^{-4}$M the mean square error and the maximum experimental error were 4 and 8%, respectively.

SUMMARY

A study has been made of the polarographic oxidation of small amounts of thiourea on a rotating platinum anode in a copper electrolyte. It has been established that when current–voltage curves are taken in a copper electrolyte, maxima are formed in the potential range + 0.10 to + 0.30 volt, these maxima being determined by the reduction of oxygen and oxidation of copper.

A direct polarographic method has been developed for determining small amounts of thiourea (greater than 1×10^{-5}M) in copper electrolytes on a specially prepared rotating platinum anode.

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*Original Russian pagination. See C.B. Translation.

BRIEF COMMUNICATIONS

ESTIMATION OF IMPURITIES IN REAGENTS DURING THE DETERMINATION OF TRACES BY PHOTOMETRIC METHODS

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During determination of traces of metals by chemical methods it is necessary to take into account impurities which are found in all the reagents which are applied,without exception [1]. In the case of the analysis of neutral salts, the question is resolved by carrying out a blank , in which the same materials as those used in the actual test, apart from the preparation itself [2] are introduced. However, when the test object is a material which is appreciably acid or basic in character, and the usually large aliquots of sample are used (5-20 g), it is almost impossible to ensure that the acidity of the test and the blank solutions is the same, and accordingly the blank test will not achieve its aim.

It is also impossible to set up a blank test when photometric methods used for determining metal impurities are applied to the water-soluble reagent itself, although in this case it is not necessary to take into account impurities contained in the components of buffer mixtures and other reagents used during the analysis. Organic materials are usually ashed [1, 3], although this procedure does not exclude possible contamination from metal vessels and from the laboratory air.

The difficulties indicated can be avoided when a single analytical result is calculated from two determinations on two different aliquots of the test preparation. This technique is particularly convenient for extraction–photometric reactions, which permit variations within a fairly wide limit in the volumes of the aqueous phase and in the amount of sample taken, without changing the volume of the organic extract. Let us examine the simplest variants of the use of this technique.

Test Object–A Neutral Salt. When m is the weight of the preparation (in g), x is the amount of impurity found in the test experiment (in μg), and y is the amount of impurity found in the blank (also in μg), then the sought-for amount of impurity in 1 g of the preparation z, is calculated as follows:

$$z = \frac{x - y}{m} \tag{1}$$

Test Object–A Material which is Acid or Basic in Character. a) The aqueous solution of the material has an acidity which is suitable for carrying out a photometric reaction.

Let the amount of impurity found in one experiment on m_1 g of test material be x_1, while in a second experiment using m_2 g of test material it is x_2. The amount of reagents used in both experiments is the same. If y is the amount of the impurity in the reagents, while z, as before, is the amount of impurity in 1 g of the preparation, then

$$x_1 = y + m_1 z$$
$$x_2 = y + m_2 z$$
$$z = \frac{x_1 - x_2}{m_1 - m_2}. \tag{2}$$

b). The acidity of an aqueous solution of the test material is not suitable for carrying out a photometric determination.

In this case it is necessary either to make the solution alkaline or acid by means of appropriate aqueous solutions of a base (ammonia, sodium hydroxide) or an acid (hydrochloric, nitric, acetic). The amount of impurity in these reagents should be determined beforehand (it should be pointed out that ammonia and hydrochloric acid are readily prepared, and can be kept free from metallic contamination by storing them in polyethylene containers [4, 5]).

When the amount of impurity in 1 ml of the neutralizing reagent is q, while for the alkalification (acidification) of two aliquots m_1 and m_2 of sample, v_1 and v_2 ml of this reagent are used, then it is possible to write:

$$x_1 = y + m_1 z + v_1 q,$$
$$x_2 = y + m_2 z + v_2 q, \tag{3}$$
$$z = \frac{x_1 - x_2 - q\,(v_1 - v_2)}{m_1 - m_2}.$$

In order to determine the amount of impurity (q) in 1 g of the neutralizing reagent, a measured volume of an aqueous solution of ammonia, nitric, or acetic acid can be evaporated to dryness, while in the case of an alkali the latter can be neutralized with hydrochloric (nitric) acid and the procedure used for the analysis of a neutral salt then followed.

Test Object—A Reagent which forms Colored Complex Compounds with Metal Ions. In this case, in order to eliminate impurities present in the components of a buffer mixture and in other reagents, it is necessary to take two equal amounts of sample in two experiments, and the volumes of all the reagents added proportionally decreased in the second experiment as compared with the first.*

Let the volume of each of the reagents in the second experiment be v_1 ml, while it is nv_1 ml in the first experiment; further let the average content of impurity in 1 ml of the mixture of added reagents be q. Then using the same designations as before for the remaining values we can write:

$$x_1 = mz + qn\,\Sigma v_i,$$
$$x_2 = mz + q\,\Sigma v_i.$$

From whence

$$q = \frac{x_1 - x_2}{(n-1)\,\Sigma v_i} \quad \text{and}$$

$$z = \frac{nx_2 - x_1}{(n-1)\,m}. \tag{4}$$

Determination of Iron in Tartaric Acid. Weights of the Aliquots taken: $m_1 = 4.5$ g; $m_2 = 0.5$g. The test materials were neutralized with ammonia (about 4 N): $v_1 = 18.9$ ml; $v_2 = 4.0$ ml. Iron content of 1 ml of ammonia: $q = 8.4 \times 10^{-3}$ μg/ml.

Determination No.	$(x_1 - x_2)$, in μg Fe	z_1, in μg Fe per g of preparation
1	7,137	1,753
2	6,873	1,687
3	7,021	1,724
4	6,853	1,682
5	7,269	1,786

$\bar{z} = 1.726$ μg Fe per g of preparation; dispersion $s^2 = 1.95 \times 10^{-3}$. Accuracy $\delta_{0.95} = \pm 0.055$. Error 3.2% (relative).

The method suggested has been designed to cover the whole concentration range embraced by the usual photometric methods (10^{-6} - 10^{-1}%); however, when there are moderate amounts of the test impurity in a sample (10^{-2} - 10^{-1}%), and fairly pure reagents are used (chemically pure or analytical grade), there is usually no need to estimate the impurity in them. It should be observed further that in order to avoid loss of accuracy during subtraction of values similar in magnitude [6] when calculating z by means of formulas (2-4), it is desirable that $m_1 \geq 2m_2$ (case 2), and $n \geq 2$ (case 3).

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* Naturally, if the determination terminates in a measurement of the optical density of an aqueous solution, then both solutions should be diluted with water to one definite volume.

In conclusion, as an example, we give in the table the results of a series of determinations of iron in analytical grade tartaric acid by means of an extraction–photometric reaction of Fe^{2+} with 1-nitroso-2-naphthol. These determinations were made by the author and A. M. Bulgakova [7]. Calculation of z_1 for each experiment was carried out by means of formula (3) given above; the results were treated statistically with a confidence level of 0.95 [8].

SUMMARY

It has been shown that it is possible to estimate the amount of an impurity in the reagents during the determination of traces of metals by photometric methods when blanks cannot be carried out; three cases are considered (the test material is acid or basic in character, or the reagent forms complex compounds with metal ions).

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A SPECTROGRAPHIC METHOD FOR THE DETERMINATION OF LITHIUM AND BERYLLIUM DURING PROSPECTING FOR THEIR DEPOSITS

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The air-blast feed method [1-3] is widely used at present in practice. Our experiments have shown that this method ensures good reproducibility for the determination of lithium and beryllium under field conditions, during prospecting for deposits of these metals (the mean error amounts to + 4.6%).

The spectrograms were taken on a ISP-28 spectrograph,using a slit width of 0.007 mm. The illuminating system was a two-lens one consisting of a UF-154 condenser (fitted on the slit) and a PS-196 with a revolver diaphragm. The opening in the diaphragm was 15 mm. An ac arc supplied from a DG-1 generator was used as the excitation source; the current was 18-20 amp and the voltage 220 volts. The spark gap was 6 mm. Spectrographically pure carbon electrodes were sharpened to a cone. The exposure time was 25 sec. The weight of the aliquots taken was 450 mg on the average.

The sand-clay material used as a dead rock for preparing standards usually contained: 59% SiO_2,22% Al_2O_3, 8% Fe_2O_3, 1% TiO_2, 3% MgO, 3% CaO, 2% Na_2O, 2% K_2O;1% of lithium and beryllium was added in the form of lithium carbonate and beryllium hydroxide respectively. Standards with contents of: 0.3; 0.1; 0.03; 0.01; 0.003; 0.001; 0.003% of lithium and beryllium were prepared by diluting the primary standard with a synthetic mixture.

Lithium was determined on the basis of the following lines: Li 6103.6 from 0.0003 to 0.01% Li; Li 3232.61 from 0.01 to 0.1% Li; Li 2741.31 from 0.1 to 1%.

Beryllium was determined on the basis of the following lines: Be 2348.61 from 0.0005 to 0.01%; Be 3130.42 from 0.003 to 0.03%; Be 3131.07 from 0.03 to 0.5%.

When lithium and beryllium were to be determined simultaneously, in addition to the photographic plates "spectrographic" type I normally used in the ultraviolet, a piece of panchromatic plate 3×9 cm with a sensitivity of 90 GOST units was introduced into the cassette in order to photograph the lithium line in the visible part of the spectrum. The iron spectrum, the spectra of 3-6 standards, and the spectra of 64-67 samples were photographed on a plate.

The spectrograms were interpreted by means of a MBS-2 microscope or by means of a spectroprojector. The analytical lines of the test elements were photometrically measured on a MF-2 microphotometer.

During the analysis of samples which vary little in their composition, satisfactory results could be obtained by using the background of the spectrogram near the test line [4,5] as the internal standard. The mean error of this method for the determination of lithium was + 10-12%, while for the determination of beryllium it was 8-10%.

Good results (an error of 7%) could be obtained by using iron as the reference element. In such cases one of the electrodes was carbon and the other iron, the lines Li 6103.64 and Fe 6137.69 were photometrically measured. Calibration curves were constructed within the coordinates: ΔS, log C.

A semiquantitative determination of lithium can be carried out by a visual method using a SLP-1 styloscope and taking the Li 6103.64 line. The visual method can be used for the determination of 0.0003-0.01% Li. A number of standards covering the lithium range indicated above were ignited beforehand by the air-blast feed method and the line intensity for each standard kept in mind. Concentrations of 0.0003; 0.001; 0.003;0.01 of Li are readily distinguished by the eye. Subsequently, using the same conditions, samples with unknown lithium contents were ignited and the lithium content estimated.

After sufficient practice it is possible to get results which are no less accurate than those obtained by the semiquantitative photographic method.

More accurate results can be obtained by introducing a reference element, which is either introduced artificially into the samples, or, what is much more convenient,a constant iron electrode is used. Both the lines being compared are evaluated visually, or are compared by means of the photometric setup of the ST-7 stylometer by a well-known method [6]. The lines Li 6103.64 and Fe 6136.62 were used for the determination of lithium.

SUMMARY

The air-blast feed method gives satisfactory results during the determination of lithium and beryllium in natural minerals.

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CHROMATOGRAPHIC SEPARATION OF HAFNIUM FROM ZIRCONIUM AND THE DETERMINATION OF HAFNIUM BY THE ISOTOPIC DILUTION METHOD

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At present there is no satisfactory chemical method for the determination of hafnium in the presence of zirconium [1]. A promising method is a combination of the methods of ion-exchange chromatography and isotopic dilution. The isotopic dilution method excludes the necessity of a quantitative separation of the component to be determined.

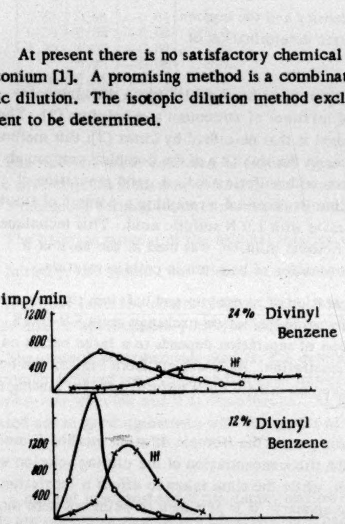

Fig. 1. Separation of zirconium and hafnium on a KU-2 cation exchange resin containing various amounts of divinylbenzene.

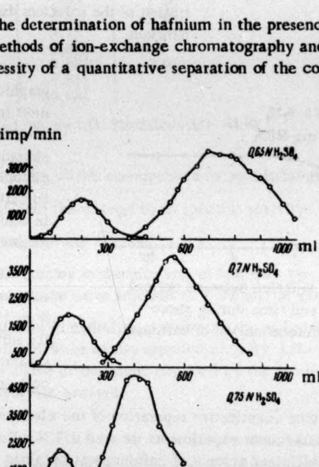

Fig. 2. Relation between the separation of zirconium and hafnium on KU-2X12 cation exchange resin and the concentration of the eluting solution (H_2SO_4).

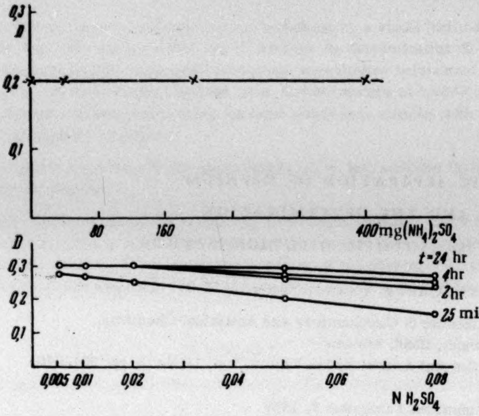

Fig. 3. The relation between optical density and the concentration of the solutions during photometric determination of hafnium.

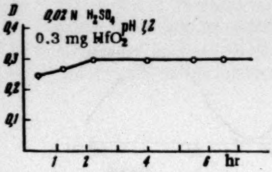

Fig. 4. Relation between optical density and time during photometric determination of hafnium.

A number of papers have been published on the chromatographic separation of mixtures of zirconium and hafnium [2]. The most interesting method is that described by Lister [3]; this method is based on differences in the stability of the complex compounds of zirconium and hafnium with sulfuric acid. A good separation of zirconium from hafnium is observed on washing a column of Dowex-50 cation exchange resin with 1.0 N sulfuric acid. This technique, in conjunction with isotopic dilution, was used as the basis of a method for the determination of hafnium in certain mixtures.

During the separation of zirconium and hafnium the best results were obtained by using the cation exchange resin KU-2X12 (Fig. 1). The sharpness of separation depends to a large extent on the sulfuric acid concentration. As is evident from Fig. 2, the best separation was achieved on using 0.65 N sulfuric acid for eluting the column.

Since quantitative separation of the element is not obligatory when the isotopic dilution method is used [4], in subsequent experiments we used 0.7 N sulfuric acid. When this concentration of the eluting solution was used a sufficient amount of hafnium was obtained in a pure form, while the time taken to effect a separation was reduced (from 18 to 13 hours—the time for the maximum to appear). It is pertinent to point out here that under the conditions adopted in [3], the maximum for hafnium appeared after approximately 50 hours.

The isotopic dilution method presumes the determination of the specific activity of the isolated compound. The radioactivity of Hf^{181} was measured on a γ-counter, using an aliquot of the solution; the activity of the standard was measured in the same way. Determination of the amount of hafnium separated was determined either gravimetrically (hafnium was precipitated in the form of its hydroxide, which was then calcined to constant weight) or photometrically by means of alizarin S on a FÉK-M apparatus. There is a published reference [5] to the effect that the acidity of the solution during photometric measurements affects the color intensity; sulfate ions also exert a negative influence on the determination. As is evident from Fig. 3, the color is constant, and is most intense at a sulfuric acid concentration of not less than 0.02 N. Sulfate concentrations within the limits 0.5-0.8 N have almost no effect on color intensity. As is clear from Fig. 4, the optical density can be measured two hours after preparing the solutions.

Analytical Procedure. An accurately measured amount of the test mixture was dissolved in a mixture of sulfuric and hydrofluoric acids on heating. The solution was evaporated and the residue of sulfates dissolved in concentrated hydrochloric acid. The hydroxides were then precipitated from this solution and filtered off; they were washed with water and dissolved in 10 ml of 2 N nitric acid. To the solution obtained was added an accurately known amount of the radioactive isotope of hafnium (Hf^{181}, $T_{1/2} = 46$ days) in the form of a nitric acid solution. The radiochemical purity of the hafnium was checked on the basis of its β-radiation. The solution thus prepared was added slowly to a small amount (approximately 1 g) of the cation exchange resin KU-2X12, a bubbler being used; approximately 75% of the mixture was thereby absorbed. The resin was then transferred to the upper part of a column 10 mm in diameter containing 10 g of the cation exchange resin KU-2X12, and the latter then washed with a 0.7 N sulfuric acid solution at the rate of 40 ml/hour.

TABLE 1

Determination of Hafnium in Synthetic Mixtures Containing Zirconium

Sample No.	HfO_2 content, %			
	taken	found	absolute error,%	error,% (relative)
1	0,50	0,46	—0,04	8,0
	0,50	0,59	+0,09	18,0
2	1,00	1,02	+0,02	2,0
		0,92	—0,08	8,0
	2,00	2,01	+0,01	0,5
3		2,07	+0,07	3,5

TABLE 2

Determination of Hafnium in Minerals

Sample No.	Amount of HfO_2, %	
	by ion exchange and isotopic dilution	x-ray spectrographic method
1	9,93	10,0
2	2,20	1,90
	2,25	2,10
3	2,25	2,25
4	0,82	
	0,86	0,95
5	0,85	
	0,88	—

---

*Carried out by I.D. Shevaleevskii

The fractions were collected in a turret type sample collector. Radiometric control of the course of the experiment ensured selection of fractions with maximum activity, which corresponded to pure hafnium.

The hafnium content of the original mixture was calculated from the change in its specific activity.

Initially, the method was checked on synthetic mixtures, using 100-mg aliquots.

It follows from the results given in Table 1 that for hafnium contents in the mixtures of less than 1%, the relative error is approximately 10%; at higher hafnium concentrations, the error amounts to 3-5% on the average.

The method described was used for the determination of hafnium in eudialite and zirconium, and also in concentrates isolated from them and in total oxides. All these samples were kindly supplied to us by I.D. Borneman-Starynkevich and V.I. Chastukhina. As is evident from Table 2, the results obtained by the method suggested are in good agreement with the results of x-ray spectrographic analysis.

SUMMARY

A method is suggested for the determination of hafnium in the presence of zirconium, in which these metals are separated on a cation exchange resin and the isotopic dilution method then used.

The results obtained for various mixtures are in good agreement with those of x-ray spectrographic analysis. The mean experimental error is 5-7%.

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DETERMINATION OF HIGH CONCENTRATIONS OF OZONE

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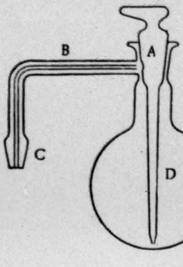
There are no published methods for the determination of high concentrations of ozone. Certain physical methods of analysis [1], in particular a spectrographic method [2] based on microphotometric measurements of the absorption band of ozone (2500 A), are of interest for the quantitative determination of ozone. Use is sometimes made of the decolorization of aqueous solutions of indigo by the action of ozone [3], or of the interaction of ozone with 4,4-tetramethyldiaminediphenylmethane, which in carbon tetrachloride solutions gives with ozone violet, amethyst, rose, and ruby-red colors [4].

The most widely used method for the determination of small concentrations of ozone is based on the absorption of ozone by a potassium iodide solution [5] according to the equation $H_2O + 2KI + O_3 = 2KOH + I_2 + O_2$. This method is very simple and convenient [6]. When, however, this method is used for the determination of high ozone concentrations a number of difficulties crop up which are determined in the first instance by the high aggresiveness of concentrated ozone. At high ozone concentrations a local increase in the alkalinity of the medium is possible in those places where the test gas comes in contact with the potassium iodide solution; in an alkaline medium the reaction then follows the equation $KI+3O_3=KIO_3+3O_2$, i.e., instead of free iodine being liberated the latter is oxidized further to yield potassium iodate [7]. This should lead, naturally, to low results; the error may be several percent. Accordingly, in order to obtain accurate results it is necessary to ensure conditions such that the oxidation of potassium iodide occurs in a strictly neutral medium. The technique described below permits one to overcome the complications indicated to a considerable extent.

The main feature of the method is the use of evacuated, tared flasks with a capacity of 200-300 ml (see figure). In a hollow ground stopper A there is a side opening with antenna-like hollows on both sides which permit ingress of the test gas at any low velocity. By means of this opening it is possible to connect the internal cavity of the flask with the side capillary opening B fused into the neck. The capillary side arm terminates in a ground joint C to which is connected the test tube containing the ozone test liquid (or vessel containing gaseous ozone). The capacity of the test tube and the capillary side arm should be as small as possible, so as to decrease the correction which has to be applied for the amount of air in them. The lower part of the stopper A ends in a thin tube D which reaches the bottom of the flask and terminates in a fine nozzle or in a coarse porous glass filter.

Into the flask is introduced 25-30 ml of 0.5 N potassium iodide solution containing a buffer mixture of the following composition: 1) 11.6 g of boric acid and 1.15 g of borax per liter of solution (pH 7.09) or 2) a mixture of the following phosphates $Na_2HPO_4 + KH_2PO_4$ (pH 6.85).

The stopper is smeared with vacuum grease (silicon or fluorocarbon polymer). The flask is stoppered in the horizontal position so that the end of the tube is not immersed in the solution. Having then connected the flask to the vacuum pump, the flask is evacuated until a residual pressure of 5-10 mm Hg is obtained (up to the point at which the solution in it starts to boil). The flask is weighed on an analytical balance by fixing it onto the hook of the balance instead of one of the weighing pans. In view of the large volume of the flask the constant



temperature of the balance room during the time between the two weighings is of considerable importance (before and after sampling). In addition, prior to each weighing, the flask is kept on the balance for 20-30 minutes. The tared, empty flask is connected to the test tube containing the test ozone (the ground joint is also smeared with grease). By rotating the stopper the flask is slowly filled with the test mixture; the rate at which the gas is passed into the flask is controlled by the rate at which the bubbles pass through the potassium iodide solution. When the gas rate is too high a cloud of iodine pentoxide is formed. After the flask has been filled it is again weighed (the grease is removed from the joint C by washing it with acetone). The increase in weight of the flask gives the amount of test mixture taken. 50-70 mg of concentrated ozone or a correspondingly larger amount of more dilute mixtures is taken for a determination. A correction for the air contained in the test tube and the capillary side tube is applied to the increase in weight of the flask; this correction is determined in a blank test. The potassium iodide solution in washed out of the flask into a 100-ml standard flask. The amount of free iodine which has been liberated is then determined by titration with 0.1 N sodium thiosulfate.

The reproducibility of the results was checked on mixtures of ozone and oxygen of constant composition. In order to prepare such mixtures, concentrated ozone was condensed at the temperature of liquid oxygen (-183°) and kept for five minutes in a vacuum at a residual pressure of 2 mm Hg, which is readily obtained by continuous pumping out with a vacuum pump (it is oxygen which evaporates mainly). The sample of concentrated ozone prepared in this way was rapidly (in the course of a few seconds to prevent condensation of atmospheric oxygen) disconnected from the pump and connected with the flask used for analysis.

Sample weight, mg:	87.8	66.6	74.6	62.4	71.4	60.2	63.8	61.2	119.4	66.0	85.4	
O_3, weight %:	97.9	97.8	98.3	97.4	97.4	97.8	98.3	96.8	97.6	97.2	98.1	(Av. 97.7)
Deviation from the mean:	+0.2	+0.1	+0.6	-0.3	-0.3	+0.1	+0.6	-0.9	-0.1	-0.5	+0.4	

Note. Variation in the temperature of the balance room during weighing was ± 0.5°.

The main sources of systematic errors are the following.

The accuracy of the iodometric titration using 0.1 N sodium thiosulfate is about $\pm 0.5 \times 10^{-5}$ mole or ± 0.24 mg ozone. 0.01 N sodium thiosulfate may be used in order to try and cut down this error.

The sensitivity limit of the analytical balance was ± 0.1 mg.

The serious source of error is the change in temperature of the balance room between the first and second weighings of the flask, since this leads to a change in the weight of the air expelled from the flask. For a flask with a volume of 200 ml the change in weight amounts to 0.9 mg for a change in temperature of 1°.

If one can eliminate the sources of error arising out of variations in the temperature of the balance room, then the maximum over-all absolute error is about ± 0.34 mg. This means that for an average weight of test mixture of about 50 mg, the maximum scatter of results should not be greater than ± 1%.

The main advantages of the method are as follows.

Instead of measuring the volume of the test mixture, its weight is determined and this excludes errors connected with measuring volumes (effect of temperature, pressure, solvent, etc.). Considerably more favorable conditions are created for absorbing the ozone by the potassium iodide solution, and due to this the deleterious effects of side reactions are decreased. Evaporation of the concentrated ozone is carried out under a vacuum at a low partial pressure; this decreases the tendency for explosions to occur during evaporation.

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POTENTIOMETRIC DETERMINATION OF SULFATE IONS

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Since there are no reliable electrodes for SO_4^{2-} [1-5]indirect potentiometric methods [6-12] have been adopted in the main; these methods are based on precipitation of SO_4^{2-} ions as $PbSO_4$ with subsequent titration of excess of the precipitant with chromate [8, 12], ferrocyanide [6], orthophosphate [9],etc. In the present article the possibility is demonstrated of carrying out a potentiometric determination of sulfate ions by titrating the excess lead ions with a solution of sodium sulfide or with thioacetamide using a sulfide electrode [13]. We have studied the determination of metals by precipitation in the form of their sulfides with thioacetamide and sodium sulfide previously [13-15] accordingly, in this article we shall simply discuss details pertinent to the determination of SO_4^{2-} ions.

Titrations were carried out by a compensation method, using a PPTV-1 potentiometer and a galvanometer with a sensitivity of 10^{-8} amp/division. A sulfide-silver electrode, prepared as described previously [13] was used as the indicator electrode. The reference electrode was a saturated calomel electrode.

Lead was precipitated with both thioacetamide and sodium sulfide. The thioacetamide solution was prepared by dissolving a preparation of the latter which had been recrystallized twice from benzene. The sodium sulfide solution was prepared from a preparation purified as described in [16]; the solution was stored in a dark glass vessel under a layer of vaseline oil. The solutions of thioacetamide and sodium sulfide were standardized against metallic lead.

The titration curves obtained with 0.01 M solutions of lead nitrate in 50% ethanol and 0.1 M solutions of sodium sulfide or thioacetamide had large potential jumps near the end point.

TABLE 1

SO_4^{2-}, g		SO_4^{2-}, g	
taken	found	taken	found
0,0144	0,0140	0,0048	0,0045
0,0144	0,0144	0,0192*	0,0195
0,0096	0,0099	0,0144*	0,0145
0,0096	0,0091	0,0096*	0,0098
0,0048	0,0047	0,0048*	0,0045

* In the presence of CO_3^{2-}.

Sulfate ions were determined as follows: to the test water,* the volume of which depended on the expected sulfate ion content,** ethanol was added*** in such amount that its concentration was not less than 25%; an accurately measured excess of 0.1 N lead nitrate or acetate was then added, followed by some more ethanol (25% of the volume of precipitant added). The solution plus lead sulfate precipitate were thoroughly mixed and after standing for 5-10 minutes were filtered through a normal paper filter. The precipitate on the filter was washed with 25% alcohol. To the combined filtrate and wash liquors was added acetic acid (until its concentration was 2%) and the solution finally titrated with sodium sulfide. When the solution was titrated with thioacetamide, hydrazine hydrate (7 ml of a 10% solution of hydrazine hydrate per 20 ml of filtrate) was added to the acidified filtrate, and the solution titrated with 0.05 M thioacetamide.

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*When the water contained carbonate ions it was acidified with a small amount of hydrochloric acid.

** The volume of H_2O to be taken was established by means of 0.1 N $BaCl_2$. If addition of $BaCl_2$ solution to the water produced only weak turbidity, then 100 ml of water was taken; if a copious precipitate formed, only 10 ml was taken.

***Other nonaqueous solvents can be used instead of ethanol, as long as they depress the solubility of lead sulfate, e.g. acetone.

TABLE 2

Test water	pH	Hardness, meq/liter	Dry residue, mg	Cl^-, mg/-/liter	SO_4^{2-} found	
					potentiometrically	gravimetrically
River Oskol on the Krasnyi Oskol	6.8	5.19	412.0	36.0	90.25	89.4
River Bakhumutka	7.8	32.09	4888.0	1140.0	1292.20	1309.2
River Gorelyi Pen'	7.55	44.36	5592.0	1160.0	2092.8	2088.9
The Donets on the Zakotnyi above the Bakhumutka	7.2	7.74	672.0	100.0	130.0	128.1
River Belaya below Ufa (50 km)	7.6	6.61	not detd.	38.4	94.2	95.2
Discharge from the Krasnovishers-kii Paper Combine	not determined				128.0	127.4
Sulfate lye from the Krasnovishers-kii Paper Combine		The same			900.0	906.0
Discharge No. 2 from the Ufims-kii Petroleum Refinery		" "	—		254.8	256.8

The reproducibility and accuracy of the determination of even small amounts of SO_4^{2-} ions are completely satisfactory (Tables 1 and 2). Chlorides, even when present in amounts 60 times that of sulfate, do not interfere. Carbonates in neutral or weakly alkaline media lead to high results. However, on acidifying the solutions to pH 4, the effect of carbonates can be completely eliminated.

Table 2 contains results for the determination of sulfate ions in water from the Donets river and its tributaries, and also in water from the tributaries of the Kama river.

SUMMARY

A method has been developed for the determination of sulfate ions which is based on their precipitation as lead sulfate, with subsequent determination of excess lead ions by potentiometric titration with thioacetamide or sodium sulfide, using a sulfide electrode.

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* Original Russian pagination. See C.B. translation.

A SIMPLE METHOD FOR THE DETERMINATION OF THE RADIOACTIVITY OF COMPOUNDS LABELLED WITH C^{14}

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The most widely used method for measuring the radioactivity of organic compounds labelled with C^{14}, consists of the combustion of an aliquot of test material (dry or wet methods) and determination of the $C^{14}O_2$ formed, either directly (in an internally filled counter) or after its conversion into $BaC^{14}O_3$, from which deposits of varying thickness are formed [1]. This method is, however, difficult, takes a long time and cannot always be used.

Recently, brief communications have appeared on some variants which are simple to carry out for the direct determination of the activity of nonvolatile organic compounds, in which uniform distribution of the test material on the whole surface of the target is achieved. All these methods are either complicated [2-4] or the descriptions given are so brief that the limits of their applicability are still not clear [3, 5].

In this connection therefore we have described in the present article a simple, rapid, and fairly accurate method which we have used for the direct determination of the relative radioactivity of various nonvolatile organic compounds labelled with C^{14}. This method is based on the use of chromatographic paper of uniform thickness, which consequently exhibits constant absorption of the soft β-radiation over its whole surface [6].

On placing a few μl of a dilute solution of the radioactive material in a suitable solvent on a disc of such paper (Whatman type), a round spot is formed, and after drying the material it is found to be almost uniformly distributed in the paper*. Thus, the paper in fact plays the role of a carrier, the thickness and weight of which are standard.

We have used this method (the direct measurement of radioactivity) for the determination of the relative activity of tropyl compounds and benzoic acid prepared from them [7]. We carried out parallel measurements of the activity of an infinitely thin layer of $BaC^{14}O_3$, obtained by wet combustion of these materials. As is evident from the results given in Tables 1 and 2, both methods give results which agree to an accuracy of up to 3%.

In addition to the compounds mentioned above, the method has also been used successfully for the determination of the activity of some other C^{14}-containing compounds: para-nitrophenylhydrazone of benzaldehyde (Table 3), dibenzhydryl ether, N-acetylbenzhydrylbenzylamine, N-phenyl-N'-benzylthiourea, N-phenyl-N'-methyl-N'-benzylthiourea, asparagine, and aspartic acid.

The following conclusions can be drawn from the results obtained (Tables 2-4).

Water and readily volatile organic solvents (alcohol, chloroform, acetone) are suitable as solvents. Despite the fact that when aqueous solutions are used the paper discs warp a little on drying, repeatable results are obtained, and water can be used with as much success as the organic solvents.

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* The chromatographic effect can be ignored.

TABLE 1

Analysis of Tropyl Salts and Benzoic Acid

Test material	Relative activity			
	measured on paper		measured as $BaC^{14}O_3$	
	cpm/ mM	%	cpm/mM	%
Tropylium bromide	5, 57·10^5	100	2, 34·10^5	100
Benzoic acid prepared from tropylium bromide	0,742·10^5	13,3	0,298·10^5	12,7
Tropylium chloride	5, 55·10^5	100	2, 31·10^5	100
Benzoic acid prepared from tropylium chloride	0,755·10^5	13,6	0,294·10^5	12,7

TABLE 2

Determination of the Radioactivity of Tropylium Salts and Benzoic Acid by Direct Measurement of Paper*

Test material	Sample wt., mg	Solvent, ml	Count rate, cpm,**	Relative activity, cpm, mM
Tropylium perchlorate prepd. from tropylium bromide	13,4	H_2O, 1	390±15	(5,57±0,27)·10^6
Benzoic acid prepared from tropylium bromide	19,4	Alc., 1	118±4	(0,742±0,025)·10^6
Tropylium perchlorate prepd. from tropylium chloride	23,7	H_2O, 1	692±6	(5,55±0,005)·10^6
Benzoic acid prepared from tropylium chloride	19,4	Alc., 1	120±5	(0,755±0,025)·10^5

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* Whatman No.2 paper was used; 11 μl of solution was placed on each target.

** The mean values obtained by measuring five targets are given

TABLE 3

The Radioactivity of Benzaldehyde-C^{14}-Nitrophenylhydrazone at Various Concentrations

Conc. of alc. soln., mM/liter	Count rate, cpm *	Relative activity, cpm,mM	Deviation from the mean, cpm, mM	Deviation from the mean, %
6,23	88±2	1,41·10^6	0,02·10^6	1,4
8,84	124±3	1,40	0,03	2,1
13,82	206±3	1,49	0,06	4,2
17,12	242±4	1,41	0,02	1,4
	Mean	1,43·10^6		

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* The mean values obtained by measuring seven targets are given; 10 μl of solution was placed on each target.

TABLE 4

The Radioactivity of Benzoic-C^{14}-Acid for Various Concentrations of the Test Solution

Conc. of alc. soln., mM/liter	Count rate, cpm *	Relative activity, cpm,mM	Deviation from mean, cpm, mM	Deviation from the mean,%
1,35	432±10	$3{,}20\cdot10^7$	$-0{,}01\cdot10^7$	−0,31
2,70	868±12	3,21	0,00	0
5,40	1735±23	3,21	0,00	0
8,10	2574±72	3,18	−0,03	−0,93
13,50	4448±110	3,29	0,08	2,5
27,0	8620±140	3,19	−0,02	−0,62
	Mean	$3{,}21\cdot10^7$		

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* The mean values obtained by measuring seven targets are given; 10 μl of solution was placed on each target.

During a comparison of the relative activity of various compounds there is no need to take equivalent amounts of them, since within definite limits there is a direct relationship between concentration and the activity. Variation in the concentration over a fairly wide range (Tables 3 and 4) leads to an almost constant value for the molar activity. However, the concentration of the solution apparently should not be too high, since crystallization of the material on the surface of the paper can occur and this is not desirable during comparison of the activity of various compounds.

The value of the specific activity measured by this method was found to be 2.5 times that obtained during determinations carried out on a thick layer.

Technique of Preparing Samples. Filter paper (Whatman No. 2) of the same diameter as the target* was placed on a target with an internal diameter of 18 mm. At the center of each disc, strictly equal volumes of a solution of the radioactive test material in a suitable solvent (about 10 μl,** 1-30 molar solution) was placed by means of an automatic micropipet. It is essential to ensure that the spots formed are similar in shape. After drying in a desiccator at room temperature the activity was measured on an end counter.

The method suggested has the following advantages.

There is no need to carry out a combustion of the test material—this considerably simplifies the work and cuts down the time; moreover, it permits determination of the activity of materials for which combustion is not possible for some reason or other (explosion hazards, incomplete combustion, etc.).

Measurements can be carried out when only small amounts of test material are available. Thus, for each determination of the activity of benzoic acid by converting it into $BaCO_3$, not less than 12.5 mg of test material is required [8], while several hundred determinations can be carried out on paper with this amount of material.

The method is 2.5 times more sensitive than measurements carried out with a thick layer of $BaCO_3$, and can in practice be used for comparing the activity of any nonvolatile organic compounds (probably with the exception of those compounds which contain heavy metals).

The method can be used for determining the activity of materials containing radiosulfur S^{35}, while if standards are available the method can also be used for measuring the absolute activity.

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* We used aluminum targets.

** When this amount of solution is used a spot is formed whose area is equal to or somewhat less than the area of the paper disc. Larger amounts of solution are not absorbed by a disc of such diameter.

SUMMARY

A simple and rapid method is suggested for preparing samples for comparing the radioactivity of nonvolatile organic compounds containing C^{14}.

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*Original Russian pagination. See C.B. Translation.

THE REPRODUCIBILITY OF THE RESULTS OBTAINED DURING THE QUANTITATIVE DETERMINATION OF AMINO ACIDS BY PARTITION PAPER CHROMATOGRAPHY

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During the quantitative determination of amino acids by means of partition paper chromatography, in most cases the amino acid content of the test material is calculated by means of standard curves. We have, however, pointed out long ago [1] that such a method leads to erroneous results. Instead of this technique, therefore, we suggested that the amount of the amino acids be determined on the basis of the ratio of the extinction of solutions of the diketohydrindylidenediketohydrindiamine formed by the interaction of the amino acids of the test and standard mixtures with ninhydrin, and developed on the same sheet of paper. Despite our suggestion, hitherto, both in Russian and foreign literature, more and more modifications of the quantitative methods of determining amino acids by paper partition chromatography based, as before, on calculation of the amino acid content from calibration curves, continue to appear. This fact has led us to publish experimental data on the problem of the reproducibility of the results and on the possibility of carrying out work on the basis of standard curves during the quantitative determination of amino acids by paper partition chromatography.

While studying the laws governing protein and amino acid metabolism in the silkworm during the period 1955-1957, we determined the amino acid content in the organism of the latter by paper partition chromatography [2]. In the course of this study hundreds of chromatograms were obtained and a large amount of numerical data accumulated, which characterized the spread in the variations in the values of the extinction of solutions of the copper salt of diketohydrindylidenediketohydrindiamine, corresponding to the same amount of amino acid placed on the chromatogram.

It was found that on taking readings from various chromatograms the amplitude of these variations was considerable. The compound square deviation for alanine, leucine and isoleucine, glutamic acid, arginine, and lysine (on the basis of an average of 54 chromatograms for each amino acid) was found to be 10.5%; while for glycine, valine, serine, threonine, histidine, and tyrosine (from 59 chromatograms) it was 15.1%; for aspartic acid, proline, and phenylalanine (from 39 chromatograms) it was 23.0%; and, finally, for cystine and cysteine (from 54 chromatograms) it was 29.6%. Such a low reproducibility of the results when the amino acid content is calculated from different chromatograms clearly points out the impossibility of using standard curves when working with paper partition chromatography.

On the other hand when special analyses were carried out using the same technique, but in which the amino acid content was calculated from the ratio of the extinction of solutions of the copper salt of the dye taken from the same chromatogram, fully satisfactory results were obtained. In this case the mean square deviation for glycine, alanine, arginine, and tyrosine (from 11 chromatograms on an average for each amino acid) was found to be 2.2%, while for leucine and isoleucine, serine, threonine, lysine, histidine, proline, and phenylalanine (from 11 chromatograms) it was found to be 5.3%.

What are the reasons for this phenomenon?

The first reason for the variation in the yield of the colored compound is the unavoidable loss of amino acid during development of the chromatogram. This loss is made up of losses suffered during absorption on the paper, losses as a result of the interaction of the amino acids with one another, or with the components of the developer, losses as a result of possible separation of the racemates of the amino acids into optical antipodes, etc.

The second important reason is the change in the sensitivity of the reaction between amino acids and ninhydrin with changes in the conditions under which the colors are developed: temperature, moisture content, type of paper used, the nature and concentration of the cations and anions present in it, the quality of the ninhydrin, the presence of oxidizing or reducing agents in the paper, the composition of the surrounding gaseous medium, the extent to which the component parts of the developer are removed from the paper, and many other factors known and hitherto unknown.

As is evident from what has been said above, the nature of the reasons leading to significant deviations in the yield of colored product during quantitative determination of amino acids by paper partition chromatography is such that attempts to alter the position by standardizing the analytical conditions do not have any foundation. Replacement of ninhydrin by hydrindantine, or construction of curves after carrying out a complete chromatographic procedure with standard solutions of amino acids, do not lead to success either.

Satisfactory reproducibility and reasonable accuracy of the results when using the method of paper partition chromatography for the quantitative determination of amino acids can only be achieved when readings are taken which characterize the standard and test mixture of amino acids from the same chromatogram; only in this case do all the operations with the amino acids of two or more mixtures being compared proceed under strictly identical conditions at all stages of the analysis.

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SEPARATE DETERMINATION OF CYCLOHEXANONE AND CYCLOHEXANONE OXIME IN AQUEOUS SOLUTIONS AND IN AIR

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Existing methods for the determination of cyclohexanone [1-3] and cyclohexanone oxime [4-6] are mainly suitable for their separate determination.

In a previous article [7] we described an improved method for the determination of cyclohexanone, which was based on its reaction with the diazonium salt of H-acid (1-amino-8-naphthol-3,6-disulfonic acid). Under the normal conditions used for carrying out the coupling of cyclohexanone with the diazonium salt of H-acid, cyclohexanone oxime is deoximated to a considerable extent. In the presence of nitrous acid, the deoximation of cyclohexanone oxime proceeds rapidly and quantitatively. When, however, materials which, according to G. Meyer [8], are capable of forming a double salt with ketoximes are added to the test solution, deoximation of cyclohexanone oxime does not occur. According to our work, thiocyanates, citric acid and its salts, sodium sulfite, and methanol could be materials of this type.

Bearing in mind the capacity of cyclohexanone oxime under certain conditions to be deoximated rapidly and quantitatively to cylcohexanone (while in other cases it hardly undergoes this reaction at all), it should be possible to use the formation of an azo dye during the coupling of cyclohexanone with the diazonium salt of H-acid for the separate determination of cyclohexanone and cyclohexanone oxime. The determination could be carried out both by the usual photometric methods, and also by colorimetric titration with a standard aqueous solution of the azo dye obtained on coupling cyclohexanone with the diazonium salt of H-acid.

The azo dye which is necessary for preparing the standard solution used in the determination by photometric titration can prepared by a procedure set out in our previous article [7].

Determination of Cyclohexanone in the Presence of Cylcohexanone Oxime. Reagents:

1. Diazo solution of H-acid. A 0.25% aqueous solution of the mono-sodium salt of H-acid in 0.1 N sulfuric acid or hydrochloric acid is mixed prior to use in the ratio of 1:1 with a 1% solution of sodium nitrite.

2. A standard solution of cylcohexanone containing 50 μg/ml is used for the photometric method by the standard series method, or a millimolar solution of the azo dye is used for carrying out the determination by colorimetric titration. The millimolar solution of the azo dye is prepared by dissolving 0.758 g of the dye in one liter of water; 1 ml of this millimolar solution of the azo dye corresponds to 0.98 μg of cyclohexanone and 1.13 μg of cyclohexanone oxime.

Analytical Procedure. To 1 ml of an aqueous solution of the sample contained in a test tube is added 1 ml of chemically pure methanol. After mixing, 0.5 ml of a 20% solution of sodium hydroxide and 0.5 ml of the diazo solution of H-acid are then added. The whole is mixed again. It is allowed to stand for two minutes.

TABLE

Separate Determination of Cyclohexanone and Cyclohexanone Oxime on the Basis of Their Reaction with the Diazonium Salt of H-Acid, by Colorimetric Titration

Taken		Found				Taken		Found			
cyclohexanone, µg	cyclohexanone oxime, µg	cyclohexanone		cyclohexanone oxime		cyclohexanone, µg	cyclohexanone oxime, µg	cyclohexanone		cyclohexanone oxime	
		µg	%	µg	%			µg	%	µg	%
2	50	2,1	110	48	96	25	25	24	96	26	104
5	45	4,8	96	46	102,2	30	20	29	96,6	21	105
8	40	7,8	97,5	42	105	—	25	—	—	24	96
10	—	10	100	—	—	35	20	34	97,1	22	110
15	35	16	106,6	34	97.1	40	15	40	100	14	93,3
20	30	19	95	31	103,3	45	10	44	97,5	11,3	113
						50	5	51	102	4,7	94

It is then diluted to 10 ml with water and measured photometrically. During the determination of cyclohexanone on the basis of its reaction with the diazonium salt of H-acid by colorimetric titration, in parallel with the test solution, 1 ml of water is taken in another test tube and the same amount of the reagents added. The blank solution is diluted to 10 ml and a standard solution of the azo dye is added dropwise until the color of the solution is the same as that of the test. At the end of the titration the volumes are made equal.

Analytical Procedure. To 1 ml of the test solution of cyclohexanone oxime contained in a test tube is added 0.2 ml of a 1% solution of sodium nitrite and 0.2 ml of hydrochloric acid 1:4. The whole is mixed, and it is allowed to stand for one minute. 0.5 ml of NaOH and Na_2SO_3 (a 1:1 mixture of a 50% solution of NaOH and a 5% solution of Na_2SO_3) is added, followed by 1 ml of the solution of diazotized H-acid. After five minutes the solution is diluted with water to a volume of 10 ml and then photometrically measured.

For calculating the amount of cyclohexanone oxime in the presence of cylcohexanone, the amount of cyclohexanone found in the test solution containing methanol is subtracted from the total amount of cyclohexanone found in the test solution, to which no methanol had been added. This difference multiplied by a conversion factor of 1.15 gives the amount of cyclohexanone oxime.

For the determination of cyclohexanone oxime by colorimetric titration, 1 ml of water is placed in a control test tube. The same amount of reagents as was added to the test solution is then added. This blank solution is then diluted with water to 10 ml and a standard solution of the azo dye added dropwise until the color of the blank is the same as that of the test solution. From the amount of azo dye used for this titration is then subtracted the amount of the azo dye solution used for the colorimetric titration during the determination of cyclohexanone in a parallel test solution without deoximation of the cylohexanone oxime, i.e., in the case where methanol is added.

7.58 µg of the azo dye corresponds to 1.13 µg of cyclohexanone oxime.

Water is used as the sorbent for the determination of cyclohexanone and cylohexanone oxime in air. The air to be tested (15-20 liter) is drawn at the rate of 15-20 liters /hour through three washers connected in series, each containing 5 ml of water.

After sucking air through the system it is disconnected. 1 ml is taken from each washer for the determination of cylohexanone, and also 1 ml from each for the determination of cyclohexanone oxime

SUMMARY

Cyclohexanone and cylcohexanone oxime can be determined separately in aqueous solutions and in air, both by the usual photometric methods and by colorimetric titration with a standard solution of the azo dye formed by the interaction of cyclohexanone and the diazonium salt of H-acid. The error for the determination of microgram amounts of cylcohexanone does not exceed 10%. The error for the determination of cylcohexanone oxime lies within 13%.

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REVIEWS AND BIBLIOGRAPHY

N. I. TARASEVICH. A TEXTBOOK ON THE PRACTICE OF GRAVIMETRIC ANALYSIS

P. Voskresenskii

Moscow University Press. Date on the wrapper 1959, on the title
page 1958. 26 bound, printer's sheets. Price 5 rubles. 30 kopecks.
Translated from Zhurnal AnaliticheskoiKhimii, Vol. 15, No. 3, pp. 378-380,
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The need for a textbook on the practice of quantitative analysis is indisputable, since the practical side of gravimetric analysis has not been treated in sufficient detail in the existing manuals. In the author's opinion the book under review should fill this gap in this particular respect. The author "has not made it his aim to replace the textbooks" (p.3) which is the reason why a lot of attention has not been given to the the theory of gravimetric analysis. It should also be noted that the seal of the MVO [Ministry of Higher Education] and the fact that it has been printed by the Moscow University Press recommends it to all.

Methodologically the "Textbook" is made up satisfactorily and meets the demands placed on it. The book contains an introduction in which the basic questions of the theory ofquantitative analysis are outlined; they include 1) the requirements that precipitates must satisfy in gravimetric analysis, and 2) chemical methods of separating elements which are used in analytical chemistry, mainly in gravimetric analysis. In the next four chapters the following topics are dealt with: laboratory equipment, general techniques in gravimetric analysis, and gravimetric determination of various elements by different methods. The final chapter is devoted to descriptions of methods of analyzing complex materials (bronze, natural carbonates and silicates).

The book is provided with the requisite reference tables.

Since questions relating to the theory of gravimetric analysis do not form the main content of the book, the brief exposition that is given should be examined particularly carefully. It should be pointed out, however, that the author has allowed a number of errors to creep in here.

The section on "Purity of Precipitates" is not very well set out. Thus, in speaking about occlusion (p.14), the author defines it as "mechanical entraining of foreign materials during the period of growth of primary particles, and the increase in size of the crystals." But the way in which this mechanical entraining occurs is not explained. One can hardly speak about " a one-type molecular structure" (p.14) as the reason for isomorphism. "Maturing of ageing" (p. 16) is incomprehensible. How can "ageing" ripen ?

To define ion exchange resins as being simply "phenolformaldheyde resins" is incorrect.

On p. 29 "Separation by Electrolysis" the author affirms that "these methods do not require that foreign materials (reagents) be introduced into the test solution etc." This is not true: A solution to be used for electrolysis is always prepared by adding some reagent or other to it in order to establish certain conditions in the medium. In fact the author himself cannot avoid "introducing foreign materials (reagents)" in the examples he has given of the electrolytic determination of certain elements (p. 159 et seq.).

In chapter 1, p. 40, and elsewhere, mention is made of "an asbestos netting". In laboratory practice, however, one usually uses metallic netting which has been treated with asbestos and not unsupported asbestos.

On the same page it is recommended that: "During evaporation of alkaline solutions in glass, they should be acidified beforehand if the experimental conditions permits this to be done". What is he talking about? What does "acidifying" an alkaline solution mean?

The author describes an obsolescent method for determining the zero point on a balance (pp. 64-65). No one uses this technique now, and instead of five readings of the deviation of the pointer only three are taken these days.

In a description of the method of relative weighing the author writes "... the density (or, what is the same, the specific gravity)" (p. 66). From an elementary textbook on physics it is perfectly obvious that density and specific gravity are far from being the same, although their numerical values are the same. Such errors are inadmissible in a textbook.

The following curious rule is given on p. 78: "12. On finishing weighing the results obtained should be written up in the laboratory notebook (and not on a separate sheet of paper, which often gets lost, and leads to loss of time)". This would appear to be correct, apart from the phrase in parentheses, which makes no sense.

Chapter II "General Techniques in Gravimetric Analysis" calls for a lot of comments. It should be pointed out, however, that it is poor editing that is responsible for the largest number of statements which call for comment. What about the following phrase, for example: "The operational technique, and the methods used in gravimetric analysis, have been created as the result of the experience of several generations of analytical chemists, which cannot be neglected" (p. 80)? Who should not be neglected: analytical chemists or the operational techniques?

Or, what does "to be free from the mechanical performance of separate operations" (the same page) mean? And what about "aimless loss of time"?

In p. 92 the author again recommends "acidifying" alkaline solutions. Should the alkaline solution have an acid reaction? On the same page the author talks about "concentration of filtrates by evaporation." There is a significant difference between "concentration" (in the sense of the amount of material contained in solution) and "concentration" (in the sense of reducing the volume of a solution to make it more concentrated).

The technique described in p. 93 is not correct: Here the author recommends heating chemical beakers with a naked flame. This should never be done.

In subsection 11 "Drying and Calcining of Precipitates" there is another completely wrong statement. Thus, the author says "The film of carbon (resin) inside the crucible, etc. (p. 101)". About what carbon on the crucible walls is he talking about? From where has it come? Usually a film of resinification products formed during the pyrolysis of cellulose settles on the crucible walls.

It would be more correct to recommend preliminary drying of a precipitate on the filter by placing the funnel with the filter still in it in the drying oven. When such a technique is used there is no need to fear that "in the case of a very wet precipitate, boiling in the crucible will occur, with sputtering" (p. 101).

In considering the cooling of hot crucibles in a desiccator, the author seems to have forgotten that the time which he recommends for cooling—30 minutes—only applies to the case when one crucible is being cooled. When several crucibles are placed in a desiccator then the cooling time must be extended considerably.

In subsection 13 "Calculation of Analytical Results" a rather confused explanation is given to the concept of "analytical multipliers and factors" (p. 103). In chapter 2 the author uses the term "analytical multiplier", while in succeeding chapters, e.g., on p. 117 he uses the "factor for calculating chlorine", on pp. 120, 122, 125, etc. "the factor for calculating etc." We think that it is best to use the term "analytical multiplier."

In subsection 14 "Checking the Precision of a Method" it is indicated that the "precision of a gravimetric analysis varies in accordance ... with the analytical multiplier, i.e., on the method" (p. 104). How is it possible to state that the analytical multiplier and the method are the same? That the analytical multiplier depends on the gravimetric form is indisputable, but that is not the same as the method of analysis.

In the same subsection there is an unpardonable error in the calculation of the analytical results: 98.88% is repeated twice instead of 99.88%.

Chapter III "Gravimetric Determinations" contains a fairly detailed description of the usual methods of analysis of barium chloride, determination of iron, aluminum, calcium, magnesium, and phosphate ions.

In a section of this chapter entitled "The Use of Organic Reagents in Gravimetric Analysis," methods are given for the determination of nickel, magnesium, aluminum, zinc, cobalt, and titanium.

In the section on "Electro-Gravimetric Determinations" methods for the electrolytic determination of copper, nickel (cobalt), and lead are described, together with internal electrolysis and electrolysis with a mercury cathode.

The fact that the author only describes macro gravimetric methods is worthy of attention. It would seem to us that nowadays when analytical chemistry is going over more and more to semimicro- and micromethods that textbooks should spend some time on this subject and instruct students in these particular methods. The semimicromethod is of great educational importance since it teaches the student to be accurate and careful in his work.

Poor editing is again a feature of the methods described. Thus, on p. 121 it is recommended "to wash off the walls of the beaker etc." There is a difference in the concepts of "washing off" and "washing". It is completely incomprehensible how one can wash off the internal walls of a beaker. One can wash off a precipitate, but not the beaker walls.

On acquaintance with the description of the gravimetric determination of iron and aluminum (p. 124 etc.) the student will get the impression that Fe^{3+} and Al^{3+} salts do not exist in solution, since, according to the description, these salts will be completely hydrolyzed, and the only function of ammonia is to neutralize the acids formed on hydrolysis. To simplify the precipitation process in this way is incorrect.

From p. 124 we learn that " rust is cleaned with fine emery cloth until it shines ". It is doubtful whether rust shines.

On p. 131 there is an incomprehensible phrase: what does "unweathered aluminum alum M/1200" mean?. Then, what does "calcined together with the still wet filter in a porcelain crucible" (p. 131) mean ? It is doubtful whether anyone has seen "incandescent" filter paper. "Incandescent" filter paper is met on p. 134, etc.

The author speaks several times of "a lightened weighing bottle" (p. 133, 170 etc.); in p. 41 where weighing bottles are described there is no mention of it. What is the student to make of this term?

In the descriptions of electro-gravimetric determinations, the author, unfortunately, does not recommend a magnetic stirrer. It is much more convenient than the usual mechanical stirrers.

Cooling a dried electrode for 1-2 minutes (p. 162) is obviously insufficient, since during such a period the temperature of the electrode will not have come to the temperature of the balance room.

It is incomprehensible what "kapferon" is referred to on p. 177.

On p. 200 the author introduces a new term "oprobirovanie" for checking the apparatus. One usually speaks of "proverka" (for checking) which is to be preferred to the term introduced by the author.

Moscow University Press has not edited this book as it should; as a result the book has lost its scientific and methodological value to a considerable extent.

N.A. IZMAILOV. THE ELECTROCHEMISTRY OF SOLUTIONS

A.P. Kreshkov

Khar'kov State University Press, 1959, 958 pp.
Printing 10,000. Price 17 rubles 80 kopecks

Soviet chemical literature has been enriched by the very valuable book of N.A. Izmailov. It is of great interest for physical chemists and analytical chemists. The book is a textbook, monographic in character, on a course in electrochemistry which the author has taught in the course of years to students and fellows at Khar'kov University. The book is an original, fundamental textbook, in which are reflected many years of study on the part of the author in the field of nonaqueous solutions of electrolytes.

Let us consider the characteristic features of N.A. Izmailov's work.

Considerable attention is given in the book to the study of nonaqueous solutions, which have acquired great importance in analytical chemistry. The author considers aqueous solutions as a special case of solutions in general.

N.A. Izmailov starts on the basis that the division of electrolytes into strong and weak only indicates the state of the electrolyte in a given solution and not its relation to a definite, always established, class of materials. The author has convincingly shown that, depending on the nature of the solvent, the same material may behave as a nonelectrolyte, can behave as a strong or a weak electrolyte, and may behave as a neutral material, an acid, a base, or a salt. In this connection the dissociation of acids, bases, and salts are considered in the book from a unified point of view developed by the author in recent years.

In contrast to most quantitative theories of the dissociation of electrolytes, which regard the solvent as a medium in which interaction of ions occurs the quantitative theory of N.A. Izmailov is primarily based on considering the interaction of ions and molecules of the dissociating material with the solvent.

In recent years, in analytical chemistry, nonaqueous titration of individual materials and multicomponent mixtures, to which methods normally used for titrating in aqueous media do not apply, has acquired great importance.

The successes achieved in recent years in the use of nonaqueous solutions in analytical practice are determined in the main by the development of the chemical theory of solutions, the bases of which have been laid by the Russian school of chemists headed by D.I. Mendeleev. The ideas of the author on the unity of the dissociation of electrolytes and the unified quantitative theory of the dissociation of electrolytes which he has developed have undoubtedly sprung from D.I. Mendeleev's teaching.

N.A. Izmailov's book "The Electrochemistry of Solutions" is an original, systematic exposition of the modern electrochemistry of solutions based on an orderly general theory of solutions developed by the author of the book. A characteristic feature of N.A. Izmailov's book is the intimate connection between scientific theory and the solution of important practical problems. It is precisely such an exposition of the modern theory of solutions that a wide circle of chemists needs.

The book under review is not free from certain drawbacks. Some of these are the large size of the book (60 printer's sheets), the presence of a considerable number of errors, the large number of mathematical formulas which are characterized by the very large variety of designations adopted in the book; enumeration of these alone takes seven pages of the text.

The book also contains some disputable statements. For example, one cannot agree with the author's conclusion that "within the limits of one natural group of solvents, a differentiating action with respect to acids or bases of different groups is not manifested" (p. 558). This position, so it seems to us, only remains true in those cases when a solvent belonging by its nature to a definite class of chemical compounds, preserves within certain limits its acid, basic, or amphoteric character. It is well known, for example, that substituent atoms, groups, or radicals affect the physical and chemical properties of a given material, though its general nature remains unchanged, and, in turn, these changes in the physical and chemical properties can lead to a change in the effect of the solvent.

The author points out that "it is not the acid itself but the product obtained from its attachment to the solvent that dissociates into ions" (p. 569, line 20 from the top). In our opinion, one cannot call HAM the product formed by the attachment of the acid to the solvent, any more than one can call it the product of the attachment of the solvent to the acid. It would be much simpler to call it the "attachment product". This in no way prevents the reader from imagining that acids dissociate, not according to Bronsted's scheme: $HA + M \rightleftharpoons MH^+ + A^-$ but according to N.A. Izmailov's scheme: $HA + M \rightleftharpoons HAM \rightleftharpoons MH^+ + A^-$.

There are some repetitions in the book which should be avoided in subsequent editions. Thus, on p. 539, and thereafter in p.555 and p.633 the author speaks of differentiating solvents.

On p. 632 (15 lines from the top) it should be pointed out more clearly that the difference between the values of log γ_0 for ions and log γ_0 for molecules is similar for acids of the same type and different for acids of different types.

It should be pointed out, however, that the drawbacks indicated are not of primary importance and do not detract from the scientific value of the book.

One can assume that a knowledge of N.A. Izmailov's book on the part of wide circles of analytical chemists will serve as a basis for a further development of the theory of analytical chemistry and chemical and physicochemical methods of analysis.

There is no doubt whatsoever that N.A. Izmailov's book is an essential textbook and reference book for teachers of physical and analytical chemistry, for workers in analytical laboratories, and for students and candidates for degrees.

CURRENT EVENTS

QUESTIONS ON ANALYTICAL CHEMISTRY AT THE XVII INTERNATIONAL CONGRESS ON PURE AND APPLIED CHEMISTRY

I.S. Sklyarenko

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At the XVII International Congress on Pure and Applied Chemistry held in Munich (Germany) at the beginning of September 1959, about 400 reports were heard at the ten sessions. Upwards of 40 reports dealt with various problems in analytical chemistry.

Reports on the determination of traces of impurities in various compounds and pure metals were the main feature among the papers on analytical chemistry. The reports of Morrison (USA) and Kemul (Poland) were of particular interest.

Morrison's report (USA) was devoted to the importance of the determination of trace impurities during the preparation of high-purity metals and semiconducting materials. In order to evaluate the efficiency of the various methods of preparing and purifying these materials, new highly sensitive methods are essential. To such methods the reporter relates radiometry and emission spectrophotometry, with preliminary chemical concentration of the impurities. The report points out the advantages and the possibilities of the use of these methods, and gives examples of results obtained during the determination of traces of impurities in high-purity metals and in semiconducting materials (Ni, W, Si, Ge, silicon carbide).

V. Kemul (Poland) read a report on the use of the "suspended drop" method for evaluating small amounts of impurities in metals. For certain ions, the sensitivity of the method has proved to be 3 to 4 orders higher than for normal polarographic determinations. The particular value of this method is the possibility of determining impurities without preliminary concentration. The efficiency of the given method has been confirmed, taking as an example samples of zinc in which traces of the following metals were determined simultaneously: In 10^{-5}%, Pb 10^{-6}%, Cu 10^{-5}%, Ti 10^{-6}% and Cd 10^{-6}%. This author has also used the "suspended drop" method for studying intermetallic compounds of mercury.

In the session on the chemistry of actinides and lanthanides Kraft (Germany) reported on a new photometric method for the determination of quadrivalent cerium by means of sulfosalicylic acid, with which it forms, in an ammoniacal medium, a yellow-brown color. By means of this method it is possible to determine 5 μg of Ce; Mn and Fe interfere. For separating actinides from lanthanides, and also for separating elements within these families, ion exchange is often used. In their report Schubert and Boyd (USA) gave information on the first (1943) ion exchange separation of plutonium, uranium, and fission products. Hewlett's report (USA) dealt with the separation of small amounts of lanthanides from appreciable amounts of americium and curium by means of an anion exchange resin in the presence of LiCl. Iron has been separated from the lanthanides and thorium on a strongly basic anion exchange resin in a hydrochloric acid medium (Veteinik, Mazatsek; Czechoslovakia). Dedek (Germany) devoted his report to the separation of thorium, uranium, and the rare earths by means of complex formation on cation exchange resins.

Comparatively few papers were devoted to extraction separation of the elements. In Fischer's report (Germany) the question of separating the rare earths by means of liquid extraction using various solvents was dealt with. Using this method the author has separated Pr and Nd and obtained high-purity erbium oxide. Other authors have used dibutylphosphate as the complexing agent for separating lanthanides and actinides (Duckert, Drets, and Simon; Belgium). A number of reports were devoted to the study of the complex compounds of the elements.

Iensovskii (Czechoslovakia) suggested the potassium salt of diperiodatocuprate and perargenate as strong oxidizing agents for the volumetric oxidation–reduction determination of Cu and Ag.

The reports of the Soviet scientists I.V. Tananaev and D.I. Ryabchikov, which were devoted to the complex formation of the rare earths were heard with great interest.

The participants at the conference were given the opportunity to get acquainted with the methods used for teaching analytical chemistry in Munich University and in the High Polytechnical School, and also visited a number of research laboratories in these institutions.

CONFERENCE ON THE ANALYSIS OF RARE AND SEMICONDUCTING ELEMENTS

(DECEMBER, 7-11, 1959, MOSCOW)

Z.I. Podgaiskaya

Translated from Zhurnal Analiticheskoi Khimii, Vol. 15, No. 3, pp. 383-384,
May-June, 1960

The conference on the analysis of rare and semiconducting elements was convened by the State Planning Commission of the USSR, the State Scientific and Technical Committee of the USSR Council of Ministers and the Academy of Sciences, USSR (The V.I. Vernadskii Institute of Geochemistry and Analytical Chemistry, The Commision on Analytical Chemistry). The conference evoked widespread interest among Soviet scientists and industrial workers, since, in connection with the development of new technics, the necessity has arisen for a critical evaluation, choice, and systematization of current methods of analyzing and determining the rare elements.

About 1000 individuals, representing 285 scientific-research institutes, industrial laboratories, and geological services located in various parts of the Soviet Union, attended. In addition, foreign scientists from China, Poland, Czechoslovakia, Bulgaria, the German Democratic Republic, and Yugoslavia were present at the Conference.

More than 150 reports and communications were read and discussed.

The plenary session on December 7 was opened with reports given by A.P. Vinogradov on "The Basis of Conditions for Impurities in Pure Metals," by N.P. Sazhin on "The Requirements of Industry with Respect to the Purity of Materials," and by I.P. Alimarin on "Prospects for Increasing the Sensitivity and Precision of Analytical Methods."

The reports of A.P. Vinogradov and N.P. Sazhin dealt with the requirements for pure materials presented by modern science and technics, and, in this connection, the necessity for increasing the sensitivity and precision of modern methods of analyzing and determining rare elements. While a sensitivity of an analytical determination of only $10^{-2}\%$ was sufficient in 1940, and approximately $10^{-4}\%$ in 1950, at present the required sensitivity has increased to 10^{-5} - $10^{-6}\%$. For certain special cases, the sensitivity of the determination of certain impurities should be 10^{-7} -$10^{-8}\%$ (the industry of semiconducting apparatuses) and $10^{-10}\%$ (thermonuclear energetics).

I.P. Alimarin in his report threw light on the basic directions in which scientific research is developing in the field of analytical chemistry with the aim of essentially increasing the sensitivity of analytical methods, their precision, and the speed with which they are carried out. He emphasized the need for developing instrumental methods of analysis.

In the sectional sessions some of the leading scientists working in the appropriate fields gave general reports on the analytical chemistry of individual elements: D.I. Ryabchikov and E.K. Gol'braikh —the analytical chemistry of thorium; I.P. Alimarin and G.N. Bilimovich—the analytical chemistry of niobium and tantalum; A.I. Busev—the analytical chemistry of indium, gallium, and thallium; D.I. Ryabchikov and V.A. Ryabukhin—the analytical chemistry of the rare earths scandium and yttrium; V.G. Goryushina—the analytical chemistry of beryllium; S.V. Elinson—the analytical chemistry of zirconium and hafnium; V.A. Nazarenko—the analytical chemistry of germanium; N.S. Poluéktov—the analytical chemistry of lithium, rubidium, and cesium; B.N. Melent'ev and A.O. Ponomarev—the analytical chemistry of titanium; D.I. Ryabchikov—the analytical chemistry

of rhenium. These reports evaluated the modern state of the analytical chemistry of elements or groupsof elements, and indicated general and actual directions to be taken in further work in these fields.

In addition to these introductory reports, scientific communications were also read at the sectional sessions on the development of methods for analyzing and determining the rare elements in various materials.

In the session on physical methods of analysis, among other reports, of particular interest was the review given by É.E. Vainshtein of the present-day state and possibilities of the development of x-ray spectrographic analysis. The report given by A.K. Rusanov and V.V. Nedler considered modern methods of spectrographic analysis and ways of increasing the sensitivity and precision of the determinations. Of interest also was an evaluation of the possibilities of using nuclear resonance in analytical chemistry, given by N.M. Pomerantsev.

The session on electrochemical methods of analysis was opened by A.N. Frumkin, who gave a general evaluation of the possibilities of using electrochemical analytical methods. A review of the modern state of electrochemical methods used in the analytical chemistry of rare elements was given in the report of O.L. Kabanova. S.I. Sinyakova also gave a report on the polarographic determination of ultramicro amounts of metals with a stationary mercury electrode and others.

R.L. Globus gave a report on the modern position and possibilities of the development of the industry of chemical reagents, at the concluding plenary session.

An exhibition of reagents used in the analysis of rare elements was staged during the conference.

It was noted during the discussions held at the conference that Soviet scientists and industrial workers have achieved major successes in the field of the analysis and determination of rare elements. The successes of spectrographic methods (the development of the "blowing" of test samples, increasing the temperature of the source) and of spectrophotometric methods should be noted. The x-ray spectrographic method has become of great importance for the determination of the rare metals. A number of new analytical methods are based on the use of radioactive isotopes and nuclear reactions (the radioactivation method, the isotope dilution method). During the determination of small amounts of impurities good results have been achieved by using oscillographic polarography and by normal polarography with concentration of the impurities on the suspended mercury drop, and also thanks to the use of organic reagents. Methods for concentrating impurities by coprecipitating them with inorganic and organic coprecipitants, and also by extraction and exchange, are being developed intensively.

As noted at the conference, the basic problem in the analysis and determination of the rare elements is to develop more sensitive, selective, simple, and rapid methods which permit impurities to be determined at concentrations down to 10^{-7} - 10^{-8}%, and also to develop rapid and reliable automatic methods for controlling the production of the rare elements and their alloys.

For attaining the highest sensitivity of analytical determinations the conference recommended that the most promising methods for further development are the emission spectrographic and x-ray spectrographic methods, the radioactivation method, and the method of isotope dilution, improvement of photometric methods, flame photometric methods, the development of polarographic, coulonometric, fluorescent catalytic methods, and ultramicro analysis. For preliminary concentration of impurities the most promising methods are coprecipitation, extraction, chromatography, ion exchange, electrolysis, distillation, and evaporation, and also zone fusion.

The conference recommended that the search for new, highly sensitive methods and for selective reagents and reactions for the determination of a number of rare elements should be stepped up; it should include the search for new, more sensitive reagents and reactions for the photometric determination of niobium and tantalum, indium and gallium, zirconium and hafnium, the rare earths, rhenium, titanium, antimony, scandium, and elements which are present as deleterious impurities in pure metals and semiconducting materials; and also include the search for new reagents for the photometric determination of germanium which would possess a high sensitivity, and would form with germanium soluble and stable colored complexes.

With the aim of improving further scientific-research work in the field of the analysis and determination of the rare elements, and of helping production laboratories, the conference adopted a resolution on publishing, as soon as possible, appropriate textbooks which are already being prepared for publication.

COMPETITIONS FOR PRIZES AWARDED BY THE ACADEMY OF SCIENCES, USSR

Translated from Zhurnal Analiticheskoi Khimii, Vol. 15, No. 3, inside back cover,
May-June, 1960

The Chemical Sciences Division of the Academy of Sciences, USSR wishes to announce that: 1) on December 6th,1960, in connection with the forthcoming hundredth anniversary of the birth of Academician N.S. Kurnakov, a competition will be held for N.S. Kurnakov Prizes to the value of 10,000 rubles, which will be awarded to Soviet scientists for outstanding work in the field of general chemistry, physicochemical analysis and its application; 2) on February 6th, 1961 a competition will be held for N.D. Zelinskii Prizes, awarded by the Academy of Sciences,USSR, to the value of 10,000 rubles, which will be awarded to Soviet scientists for outstanding scientific work in the field of organic chemistry and chemistry of petroleum.

Materials for the competitions should be sent to the Chemical Sciences Division, Academy of Sciences, USSR not later than three months prior to the date on which the appropriate prizes will be awarded.

Address of the Chemical Sciences Division:

Moscow, B-71, Leninnskii Prospekt, 14.

Organizations and private individuals who wish to nominate candidates for the prizes should send to the Chemical Sciences Division the following documents and materials with the inscription "For the competition for the . . . Prize".

a) Published scientific work, materials appertaining to scientific discoveries or inventions; three copies in any language:

Note. Work which has already been awarded any prize will not be considered.

b) Materials presented for discussion by a Scientific Society.

c) Author's thesis not exceeding 0.25 authors sheets *

d) Brief biographical information on the candidate with a list of his main scientific work, discoveries, and inventions.

Chemical Sciences Division,
Academy of Sciences, USSR

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* As in original – Publisher's note.

CONFERENCE ON ORGANIC ANALYSIS

The Commission on Analytical Chemistry, Academy of Sciences, USSR in conjunction with the Chemistry Faculty of the M.V. Lomonosov Moscow State University intends to convene toward the end of 1960 in Moscow a conference on organic analysis.

Reports on the following questions will be read and discussed at the conference:

1. Methods of heteroorganic analysis;

2. Methods of chemical functional analysis and identification of organic compounds;

3. The use of physicochemical and physical methods (electrochemical, optical, chromatographic, etc.) for the analysis of organic materials;

4. Mass-spectrographic methods of studying organic compounds;

5. Radiochemical methods of studying organic compounds. Main attention will be focused on the problem of analyzing high molecular weight compounds, various organic polymers, and express methods of analysis.

The Commission on Analytical Chemistry and Chemical Faculty of Moscow State University invite workers in scientific-research institutes, higher education establishments, and industrial laboratories to participate in the work of the conference.

The subjects and annotated reports (4-5 typewritten sheets) as well as requests for tickets should be sent to the organizing committee at the following address: Moscow, B-133, Vorob'evskoe Shosse, 47a, V.I. Vernadskii Institut Geokhimii i Analiticheskoi Khimii, AN SSSR.

The exact date date of the conference will be published later.

Organizing Committee

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	**Phys. Inst. Acad. Sci. USSR.**
GDI	**Water Power Inst.**
GITI	**State Sci.-Tech. Press**
GITTL	**State Tech. and Theor. Lit. Press**
GONTI	**State United Sci.-Tech. Press**
Gosenergoizdat	**State Power Press**
Goskhimizdat	**State Chem. Press**
GOST	**All-Union State Standard**
GTTI	**State Tech. and Theor. Lit. Press**
IL	**Foreign Lit. Press**
ISN (Izd. Sov. Nauk)	**Soviet Science Press**
Izd. AN SSSR	**Acad. Sci. USSR Press**
Izd. MGU	**Moscow State Univ. Press**
LEIIZhT	**Leningrad Power Inst. of Railroad Engineering**
LET	**Leningrad Elec. Engr. School**
LETI	**Leningrad Electrotechnical Inst.**
LETIIZhT	**Leningrad Electrical Engineering Research Inst. of Railroad Engr.**
Mashgiz	**State Sci.-Tech. Press for Machine Construction Lit.**
MEP	**Ministry of Electrical Industry**
MES	**Ministry of Electrical Power Plants**
MESEP	**Ministry of Electrical Power Plants and the Electrical Industry**
MGU	**Moscow State Univ.**
MKhTI	**Moscow Inst. Chem. Tech.**
MOPI	**Moscow Regional Pedagogical Inst.**
MSP	**Ministry of Industrial Construction**
NII ZVUKSZAPIOI	**Scientific Research Inst. of Sound Recording**
NIKFI	**Sci. Inst. of Modern Motion Picture Photography**
ONTI	**United Sci.-Tech. Press**
OTI	**Division of Technical Information**
OTN	**Div. Tech. Sci.**
Stroiizdat	**Construction Press**
TOE	**Association of Power Engineers**
TsKTI	**Central Research Inst. for Boilers and Turbines**
TsNIEL	**Central Scientific Research Elec. Engr. Lab.**
TsNIEL-MES	**Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants**
TsVTI	**Central Office of Economic Information**
UF	**Ural Branch**
VIESKh	**All-Union Inst. of Rural Elec. Power Stations**
VNIIM	**All-Union Scientific Research Inst. of Metrology**
VNIIZhDT	**All-Union Scientific Research Inst. of Railroad Engineering**
VTI	**All-Union Thermotech. Inst.**
VZEI	**All-Union Power Correspondence Inst.**

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

DERIVATIVE POLAROGRAPHY ON SOLID ROTATING ELECTRODES IN MOLTEN SALTS*

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July-August, 1960
Original article submitted June 15, 1959

Several metals are obtained by the electrolysis of molten salts; accordingly, the study of the electrochemical properties of the impurities which accompany them is of considerable interest. When several components are present in the molten salts and ordinary polarography is employed, it is not always possible to establish the nature and the concentration of these impurities; when, however, derivative polarography is used, this becomes possible. Skobets was the first to obtain derivative peaks for several materials in aqueous solutions [1], and Chovnyk [2] was the first to obtain such peaks in molten salts.

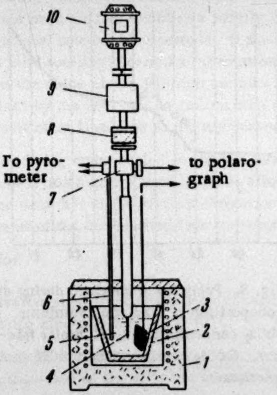

Fig. 1. Schematic diagram of the polarographic cell. 1) Electric oven; 2) porcelain crucible; 3) anode, a Pt disc; 4) cathode, a Pt wire; 5) electrolyte – supporting electrolyte; 6) thermocouple; 7) slip ring; 8) electric insulator sleeve; 9) four-stage reducer; 10) synchronous motor.

The aim of the work described in the present article was: the determination of the decomposition potential of several metal chlorides, the study of changes in the value of the diffusion currents with changes in the rotational speed of the electrodes, and also the study of changes in the nature of the polarization curves with the polarization rate.

EXPERIMENTAL

The test materials were silver, lead, and cadmium chlorides.

A eutectic mixture of lithium and potassium chlorides was used as the supporting electrolyte [3]. The polarograms were recorded on a Heyrovsky-type polarograph. A feature of this polarograph is that in addition to having the usual setup, it also has a differential setup.

The galvanometer sensitivity was $1.6 \cdot 10^{-9}$ amp/mm. The experiments were conducted at 400°. The temperature was kept constant to within ±2° by means of a thermoregulator.

A 100 ml porcelain crucible was used as the electrolytic cell. A platinum wire with a cross section

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* Presented at the analytical session of the VIII Mendeleev Conference, March 21, 1959, Izd. AN SSSR, Moscow, p. 48.

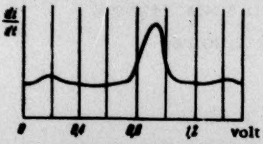

Fig. 2. Derivative peak obtained during deposition of silver in a supporting electrolyte of LiCl − KCl; AgCl concentration 0.001 molar fraction.

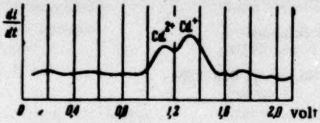

Fig. 3. Derivative peak obtained during deposition of cadmium in a supporting electrolyte of LiCl − KCl; $CdCl_2$ concentration 0.0007 molar fraction.

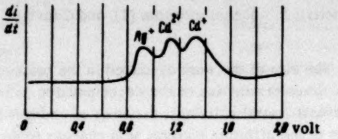

Fig. 4. Derivative peaks obtained during codeposition of lead and cadmium in a supporting electrolyte of LiCl−KCl; $PbCl_2$ concentration 0.0005 molar fraction; $CdCl_2$ concentration 0.0005 molar fraction.

of 1 mm and 8 mm long was used as the cathode; the anode was a platinum disc with a surface area of 4 cm². The electrode was rotated at speeds of 100, 500, 750, and 1500 rpm by the means of a synchronous motor operating through a four-stage reducer.

The polarographic setup is shown schematically in Fig. 1.

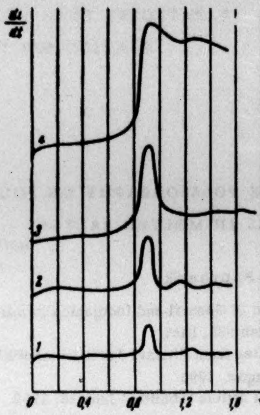

Fig. 5. Derivative peaks obtained on a platinum cathode; AgCl concentration 0.0005 molar fraction. 1) On a stationary cathode; 2) on a rotating cathode; V = 100 rpm; 3) on a rotating cathode; V = 500-750 rpm; 4) on a rotating cathode; V = 1500 rpm.

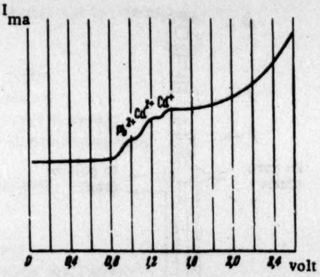

Fig. 6. Polarogram obtained during the codeposition of lead and cadmium; $PbCl_2$ concentration 0.003 molar fraction; $CdCl_2$ concentration 0.0005 molar fraction.

First of all we took ordinary polarograms for separate and simultaneous deposition of the metals in the LiCl−KCl supporting electrolyte; the concentration range examined was 0.0002-0.001 molar fractions; the sensitivity was S = 1/5000 (the additional shunt connected in parallel with the galvanometer had a value of 100 ohms). During separate deposition of the metals, reproducible polarograms were obtained; during simultaneous deposition, however, positive results were not obtained. The decomposition potential of the supporting electrolyte was −2.3 volts. The half-wave potentials were as follows: for silver, −0.9 volt; for lead −0.95 volt; two waves were obtained during reduction of cadmium chloride; the half-wave potential of the first was −1.1 volt, while for the second it was −1.3 volt. The stepwise reduction of cadmium chloride can be explained by the presence of the subchloride in solution; it has been shown that the latter can be formed both in aqueous and in molten media [4, 5]. The first wave, in our opinion, corresponds to the reduction of cadmium chloride to the subchloride, while the second corresponds to the reduction of the subchloride to cadmium metal.

The value of the limiting diffusion currents for concentrations of 0.001 molar fraction was as follows: for silver 0.24 ma, for lead 0.32 ma; for the first cadmium wave 0.16 ma and for the second 0.06 ma.

The value of the limiting diffusion current was found to be directly proportional to the concentration of the material being reduced.

The derivative polarograms were taken at a sensitivity of S = 1/200.

Initially, separate deposition of the metals on stationary electrodes was studied; the derivative polarograms obtained, in comparison with the ordinary polarograms, gave characteristics which were more clearly defined, both qualitatively and quantitatively, for the test material.

In Fig. 2 is shown a derivative polarogram for silver with a concentration of 0.001 molar fraction; a similar polarogram is shown for lead; for cadmium, as was the case on the ordinary polarogram, two waves were obtained as can be seen in Fig. 3. The potentials of the derivative peaks of the chlorides tested correspond to the values of the half-wave potentials, with insignificant deviations.

The derivative peaks obtained during the codeposition of silver and cadmium are shown in Fig. 4; a similar polarogram was obtained during the codeposition of lead and cadmium.

Our experiments on the rotating cathode, as compared with the stationary electrode, showed that at rotational speeds of 100 rpm/min the height of the derivative peak was twice that obtained on a stationary electrode while at rotational speeds of 500-750 rpm and 1500 rpm, the peaks were respectively three and four times greater than that obtained on a stationary electrode. The derivative polarograms are shown in Fig. 5.

A number of research workers have attempted to show that there is some relationship between the height of the derivative peak and the rotational rate [6, 7]; however, both the authors indicated, and our own investigations have not been able to establish a strictly mathematical relation between the height of the derivative peak and the rotational rate of the electrode. It should be noted that in aqueous solutions, the value of the diffusion currents on solid rotating electrodes (at rotational rate of 700-800 rpm) increases 15-20 times [8], accordingly, in molten salts the value of the diffusion currents is 5-7 times less than in aqueous solution. Apparently, this could be determined by the fact that in molten salts the temperature is the predominating factor. It is known that the diffusion coefficient is related to the temperature by an order relationship.

Since, during codeposition of the test ions of the metals on ordinary polarograms we were unable to obtain positive results, polarograms were taken at a low polarization rate of 10-20 mv/min; it was established as a result of these tests that at the given polarization rates on the ordinary polarogram shown in Fig. 6, the limiting diffusion currents of the codeposited ions are recorded, and the stepwise reduction of cadmium chloride is confirmed.

SUMMARY

Derivative polarograms have been obtained for the successive deposition of silver, lead, and cadmium ions in a supporting electrolyte of LiCl−KCl.

It has been established that on using a rotating solid electrode at rotational speeds of 100, 500-750, and 1500 rpm, the value of the diffusion currents increases two, three, and four times, respectively.

It has been established that limiting currents can be recorded during the codeposition of the metals, when low polarization rates are used during the recording of normal polarograms.

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SOME NITROPHENYLOSAZONES AND NITROPHENYLHYDRAZONES AS INDICATORS AT HIGH pH VALUES

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July-August, 1960
Original article submitted July 2, 1958

A systematic study of nitrophenylosazones and nitrophenylhydrazones [1, 2] has led us to conclude that these compounds could be used as indicators at high pH values. The compounds which exhibit the most clear-cut color change over a comparatively narrow pH range are the p-nitro- and 2,4-dinitrophenylosazones of dihydroxytartaric acid and the 2,4-dinitrophenylhydrazones of pyroracemic acid and acetone (Table 1). The syntheses of these materials have been described in the literature [3-5] and can be realized readily.

TABLE 1

Approximate Color Change Range of Indicators of the Hydrazone Series

Indicator	Color		Color change range in pH units
	Acid form	Alkali form	
p-Nitrophenylosazone of dihydroxytartaric acid	Light yellow	Dark blue	12.6-13.5
2,4-Dinitrophenylosazone of dihydroxytartaric acid	The same	Light violet	12.3-13.3
2,4-Dinitrophenylhydrazone of pyroracemic acid	The same	Red or dark rose	11.9-12.9
2,4-Dinitrophenylhydrazone of acetone	The same	The same	11.6(11.5)-12.6

One of the positive features of indicators of the hydrazone series is the absence of an appreciable alcohol, protein, and temperature error within certain limits. Experiments which we have carried out have shown that high alcohol concentrations (up to 60-70%) have no effect on the indicator properties. The effect of proteins was studied by means of gelatin solutions, the volume of which was altered within wide limits. During these experiments the test solutions were either completely transparent or turbid, but, nevertheless, the range over which the color changes occurred did not change. Variations in temperature from zero to 80° had no effect on the indicator properties.

The salt error (the effect of sodium chloride and potassium sulfate was studied) only becomes apparent at high salt concentrations, or more accurately, in saturated solutions. In this case at a ratio of NaCl/NaOH = 4:1 and higher, the color change range shifted by about 0.2 pH units toward the higher values; this shift was half as much for potassium sulfate.

In addition, the effect of cations of the II-IV groups of the analytical groups on the behavior of indicators

TABLE 2

Determination of pH with Indicators of the Hydrazone Series

pH	Color of solutions		
	2,4-Dinitrophenylhydrazone of acetone	2,4-Dinitrophenylosazone of dihydroxytartaric acid	p-Nitrophenylosazone of dihydroxytartaric acid
11.5-11.6	Yellow	Yellow	Yellow
11.7-11.9	Yellow with orange tinge	The same	The same
12.0-12.2	Pale orange with slight rose tinge	The same	The same
12.4-12.5	Rose with orange tinge	Indistinct orange-rose	Yellow
12.6-12.8	Dark rose with slight brownish tinge	Rose	Dark yellow with a grayish tinge
12.8-13.0	The same	Rose with slight lilac tinge	Gray with pale-orange tinge
13.0-13.1	The same	Lilac-rose	Gray with blue tinge
13.2-13.4	The same	Bright violet	Dark blue with gray tinge (appears after 2-3 minutes)
13.5 and more	The same	Bright violet	Bright dark blue

was examined, since it has been noted in the literature that there is a possibility of an interaction between certain phenylosazones and hydrazones with the ions of a number of metals [6-8]. The experiments showed that Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Ag^{+}, Cd^{2+} ions and some other ions, at concentrations up to 1 M, can be present. The hydroxides of these metals do not interact with the anions of the indicators in an alkaline medium. Mg^{2+} and Ni^{2+} ions unconditionally interfere, since their hydroxides absorb the indicator anions in an alkaline medium to form precipitates which are violet or red-violet in color.

A feature of the indicators described which is of practical importance, proved to be the invariability of the colors of the acid form in solutions of sodium or potassium carbonate (1 N and lower), ammonium hydroxide (6-7 N and lower), sodium phenolate and a number of the other salts of the alkaline metals with organic acids, which, as a result of hydrolysis, have an alkaline reaction. It is quite obvious that this property is explained by the location of the transition range; accordingly, the compounds described above, in particular the p-nitro- and 2,4-dinitrophenylosazones of dihydroxytartaric acid, can be used (as our experiments have shown) for the determination of sodium hydroxide in various materials by direct titration. For titration 0.05% alcoholic solutions of the indicators should be used, since they are only sparingly soluble in water. 0.1 ml of the indicator solution is added to each 5-10 ml of solution to be titrated. It is best to use 1 N hydrochloric acid as titrant (sulfuric acid of the same normality can be used) and to titrate until the color of the alkali form of the indicator changes over to the color of the acid form, which is yellow for all the indicators. Instead of the 2,4-dinitrophenylosazone of free dihydroxytartaric acid it is more convenient to use the osazone of the mono-substituted ammonium salt which is obtained without any difficulty by treating the freshly prepared osazone with a solution of ammonium hydroxide [2]. When the p-nitrophenylosazone of dihydroxytartaric acid is used, alcoholic solutions of this indicator should be prepared prior to use and should not be kept for more than three days [2], or solutions in other organic solvents (benzene, carbon tetrachloride) can be used.

Indicators of the hydrazone series can be used also for the photometric determination of pH in the range 11.5-11.6 and 13.4-13.5 with an error of 0.1-0.2 pH units.

Technique for pH Determination. A series of test tubes of equal diameter and made of colorless glass are chosen, and placed in a stand against a white background. 0.05% alcoholic solutions of the indicators are prepared and 0.1 ml of a solution of the 2,4-dinitrophenylhydrazone of acetone introduced into one of the test tubes, 10 ml of the test solution is then added. When the color of the latter is bright yellow, then the pH is less than 11.5-11.6, while if it has a slight orange tinge then the pH lies within 11.7-11.9. At pH 12-12.2 the color of the solution is a bright orange with a rosy tinge, while at pH 12.4-12.5 it is rose with an orange tinge. At a pH higher than 12.5 (12.7-12.8 and higher) the color of the solution is rose with a slight brownish tinge and does not change for further increases in the pH value. At high alkali concentrations (6 N and higher) the solution again becomes yellow. In order to get an accurate value for the pH it is necessary to use solutions of the same concentration of the p-nitro- and 2,4-dinitrophenylosazones of dihydroxytartaric acid; the same volumes of the two indicators (0.1 ml) are added to separate test tubes containing the test solutions.

The colors of solutions of the indicators and the pH values corresponding to them, when the conditions indicated above are used, are given in Table 2.

SUMMARY

The indicator properties of certain nitrophenylosazones and nitrophenylhydrazones have been studied, and the possibility has been established of using them in solutions with high concentrations of salts, ethanol, and protein (gelatin) within the temperature range 0 to 80°. It is suggested that they can be used for pH determination in the range 11.5 to 13.4, and for the direct titration of sodium hydroxide in a number of materials.

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* Original Russian pagination. See C. B. translation.

MICROANALYSIS, THE CHEMICAL ANALYSIS OF TOMORROW*

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When one traces the development of chemical analysis during the last four centuries, it becomes obvious that the amount of material used for analysis is continuously decreasing. Gravimetric analysis, for example, arose in the middle of the sixteenth century as the result of the work of the metallurgists Agricola and Biringucho, who reproduced on a small scale, using several kilograms of ores, the metallurgical processes of that time, in order to forecast the yield of pure material. It is known that around 1700, Homberg, who was the first to study the stoichiometric laws, carried out analysis with amounts of material of the order of 20-30 g. In the middle of the eighteenth century, Black, who was a contemporary of Lomonosov, and together with the latter, but independently, discovered the law of the conservation of matter, was already working with amounts less than ten grams. Around 1825, in the period of the blossoming of chemical analysis, thanks to the work of Gay-Lussac and Berzelius, the amount of material necessary for analysis had fallen to less than one gram. In the course of the nineteenth and twentieth centuries this amount approached 100-200 mg, which is characteristic of the amount used for modern macroanalysis, described in the classical work of Fresenius and Treadwell.

This brief review shows that gravimetric microanalysis is not the result of a normal evolutionary development.

When, around 1900, Nernst and his co-workers started to work with amounts of one milligram and less, this was a completely revolutionary idea. During further development a tendency was observed which was directly contradictory to that mentioned earlier. The amount of test material started to increase gradually. Microanalysts of the classical Austrian school Emich, Pregl, Dubský, et al., during the period 1915-1920, and at present, prefer to work with amounts of 1-5 mg, and in modern semimicroanalysis, which is more and more replacing microanalysis in the strict sense of the word, 5-15 mg of test material is used.

In general terms the same can be said of macro- and microqualitative analysis. Although no accurate data are available, nevertheless, it is known that here again the amount of test material used has gradually decreased in the course of the last three centuries. It can be accepted that the development of macroqualitative analysis started from the middle of the seventeenth century thanks to the work of Boyle, who was the first to use what we nowadays call "reagents", i.e., materials with the aid of which it is possible to detect the presence of some other material. At the end of the eighteenth century Bergman used hydrogen sulfide and the alkali metal sulfides for separating the metals into a small number of "groups." In the course of the nineteenth century, Klaproth, Rose, and, particularly Fresenius, and in the twentieth century Treadwell also, gave to qualitative macroanalysis its modern aspect.

Here again qualitative microanalysis was essentially a new method; it developed completely independently of qualitative macroanalysis. As long ago as 1679 Leewenhoek from Delft, the founder of microbiology, presented to the Royal Society of London an article "On the Figures of Salts," in which he showed that a large number of the salts known at that time can be readily identified by observation under the microscope. This fundamental idea – the germ of "microcrystalloscopic qualitative analysis" – was carefully nurtured by the naturalists of the first half of the nineteenth century, particularly by the Frenchman Raspail and the Dutchman Harting, and was developed further by Boricky from Prague and Haushoffer from Munich, and reached completion in the form of a finished "system" thanks to the work of Behrens from Delft. Since that time many reactions have been improved, and many new reactions discovered as the result of the latest research including that of Chamot and Mason in the USA, Geilmann in German, and Malyarov in Russia, but the method in its main features has remained almost unchanged.

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* Translated from English by Z. I. Podgaiskii.

Right up to 1925, the microcrystalloscopic method was the only well-known, or at least the most widely used technique in qualitative microanalysis. The next to appear were "spot reactions" or "spot tests", which, even if they were not discovered by Feigl, were first systematically studied and used by him. Thanks to research carried out all over the world, a large number of useful spot reactions were discovered in an unusually short time. Of the older Russian analysts, a very active part in the development of this field of analytical chemistry, was played by N. A. Tananaev, A. S. Komarovskii, N. S. Poluektov – the leading scientists of their time. This method not only opened up new possiblities for the identification of various ions, but also led to the present revolution in qualitative analysis, by changing the apparatus used; spot reaction plates or pieces of filter paper instead of test tubes, centrifuges instead of filtering apparatus, etc.

When, however, one turns to titrimetric microanalysis, its historical development took a totally different path. It might even be said that this analytical method hardly has any real history. In fact it has developed very recently. Even a few years ago, despite the availability of microburets, no one used them unless forced to, for example, when large amounts of material were not available. We shall return to this point later.

All that has been said above was designed to show that right from the beginning microanalysis was a method completely different from macroanalysis. It was, and very often still remains a "special method" of chemical analysis carried out by a separate group of analysts who are called microanalysts, if not microfanatics. Many analysts unwillingly tolerate it, suffer it, since it has applications in certain cases, in particular, in organic analysis. The main purpose of this article is to defend the thesis that this technique is not only a special method, but that it is definitely the best method, and that in a comparatively short time, microanalysis will be the normal method in most cases.

Of course, I cannot but take into account the fact that gravimetric and titrimetric quantitative methods of analysis are being replaced to an ever-increasing extent by instrumental methods, and that even in qualitative analysis, spectroscopy will probably replace a large number of the methods which are in current use, but this is a special question. I have no doubt myself that for at least many years to come "classical" methods of analysis will be used fairly widely, and our problem is to carry them out in the best possible way. It should be noted that spectroscopy is a typical microanalytical method, and the same can be said of many other quantitative instrumental methods. We shall not, however, discuss them here.

As for qualitative analysis, it seems to me that the advantages of microanalytical methods have already been demonstrated in practice not only in industrial research, but particularly in teaching students the bases of chemistry. Complete disorder, dirty benches, senseless waste of reagents, and unfortunate waste of time and materials are, or should be, things of the past. Thanks to the proper choice of microcrystalloscopic and spot reactions for the identification of various ions, it is possible at present even for the beginner to carry out a complete qualitative analysis with not more than 5-10 mg of test material. This has been successfully realized for a long time in the Institute of Microanalysis at Delft Technical University, and by giving a microanalytical course annually during the vacation, this technique has successfully penetrated into the practice of industrial and other research laboratories. This technique not only gives better results in a shorter period, and at a lower cost, but has the added advantage that it trains the student to be accurate and elegant in his work, which I regard as very important. Students, particularly in the first year, must be taught that chemical work should be carried out accurately, and if necessary even carried out on a dining table. I am aware that even now there are still universities in which the old methods are still adhered to. Presumably, in such universities, it is thought that microanalysis is more difficult to carry out than analysis by outdated methods, and that the students are happy if they can splash about to their hearts content. I can assure you that nothing is further from the truth; even completely inexperienced students readily get accustomed to qualitative microanalysis.

I have just written that in choosing appropriate reactions for identification purposes it is necessary to use both microcrystalloscopic and spot reactions. There is a fairly large number of scientists who seriously discuss which of these two groups of reactions is the most effective. Thisseems to me to be a futile question. It is obvious that for some ions one group is preferable, while for others the other group is more suitable. The two methods should therefore be studied. Moreover, the reliability and confidence in an identification increases when it is possible to confirm it by two different methods.

I could not possibly affirm that at present qualitative microanalysis has already reached its final and complete form. For the identification of a fairly large number of ions we should definitely like to have better, and, in particular, more selective reactions. It is quite possible that methods which will be essentially new will appear. Maybe chromatography will be used more widely than at present, etc. Until recently analysts have neglected, if not deliberately ignored, a large number of the less widely distributed elements to the detriment of the solution of geochemical and technical problems. Thus, there are still new and interesting fields to confront the present-day worker. However, even now, qualitative microanalysis has been developed to such an extent that it can replace outdated methods in those fieldswhere it can be used.

Over a period of many years the main difficulty in gravimetric microanalysis has been the problem of weighing. It cannot be denied that weighing to an accuracy of six decimal places on balances of the Kuhlmann type, as recommended by the Austrian school,is highly undesirable and tedious. Bearing in mind vibrations, the zero shift, the asymmetric heating of the balance beam, and a large number of other obstacles, weighing was really a very tense operation, and I would not be surprised if the antipathy often found toward microbalance procedures has not found conscious or unconscious justification in these Kulman balances.

But all this is past history. Modern, completely automatic balances have, in practice, put an end to the difficulties of weighing, particularly if one can be satisfied with the fifth decimal place for ordinary work, and where weighing to the sixth place has only to be carried out in those rare instances where it is unavoidable. In the past, without any doubt, there were too many microfanatics, who weighed to microgram accuracy when there was no real need, and what is worse, without having any clear ideas of the precautionary measures which are necessary in such cases. I shall mention two such cases. The first only relates to Kuhlmanbalances. It has always been considered that calibration of the weights is not essential, since the difference between the weight of an empty and a full crucible was determined from the notches on the balance arm or from the scale. But it was forgotten that it is more difficult to place the notches at exactly equal intervals than to ensure an exact equilibrium, and that, in each case, calibration of the weights however tedious it might be, is considerably easier than calibrating the notches on the balance arm. The second difficulty which is not normally taken into account, consists in the changes in air density which must be considered when a Kuhlmann balance or an automatic balance is used. It is usually assumed thatArchimedes' force can be ignored, since it is the same for the empty and the full crucible; but, this is only true in those cases where the air density does not change in the time interval between the two weighings. It can be calculated that for rapidly changing atmospheric conditions, neglect of this fact can easily lead to errors of 40-30 μg. Some even advance this fact, without any foundation,in my opinion, as an argument against the use of automatic one-pan balances. I have shown [1] that by using a simple apparatus which follows changes in air density, that the source of these very considerable errors can be readily eliminated by rapidly reducing the results of all weighings to the same temperature and atmospheric pressure. We have established that it is possible in this way to increase the precision of microgravimetric determinations significantly.

In general, it seems to me that,at present, weighing to the fifth or even sixth decimal place on a completely automatic balance is not more difficult, and takes no longer, than weighing to the fourth place on the old-type balances with or without damping.

Bearing this fact in mind, one can hardly deny that gravimetric microanalysis has many advantages. Above all it is appreciably quicker than the macromethod. It can be readily shown, and experiment has confirmed this, that the time necessary for many tiresome analytical operations, e.g. dissolution, evaporation, and filtration decrease by approximately 50% when the amount of material is reduced to a tenth. Where time is money, the micromethod is the answer. Secondly, the micromethod is cheaper from the point of view of reagent expenditure. By cutting down the amount of material to a tenth, an economy of 90% on the reagents can be effected. If cost is not of primary importance, then taking the cost by a macromethod as an operational level, then it is is possible, using a micromethod, to use better but more expensive reagents. Thirdly, the micromethod requires much less laboratory space, and this can be of decisive importance under certain conditions. Finally, work on a microscale can be carried out by more elegant techniques, which, on the one hand is very desirable for instructing students, and on the other hand, is a guarantee against slovenly work in industrial laboratories.

Finally, all that has been said would not be of great significance if microgravimetric methods were considerably less accurate than macrodetermination. At the moment, in our opinion, microanalysis cannot ensure such a high degree of accuracy as is possible by using a macromethod. Actually, it cannot be denied that in order to achieve the highest accuracy, it is necessary to increase rather than decrease the amount of sample used. But microanalysis is a comparatively new method, it is not surprising that hitherto it has not always been able to compete with macroanalysis, which already has a history of 200 years behind it. Moreover, very often the "notorious" accuracy of the ordinary methods is nothing else than a high degree of reproducibility, while the errors — deviations from the true value — are masked by standardization. In many other cases, high accuracy — only an unnecessary increase in the qualificationsof laboratory workers — is unjustified both from a scientific and an industrial point of view. All the same, at present, the accuracy of microanalysis is only slightly less than that of macroanalysis. There is a basis, however, for assuming that finally this small difference will disappear.

In this connection I shall deliberately not use the term "semimicro" since it can lead to confusion. In our institute we arbitrarily designate as "semimicro" all those gravimetric methods in which weighing is carried out to the fifth decimal place, and as "micro" those methods where the weighing is carried out to the sixth decimal place — independently of the amount of material. Thus, in this sense I of course acknowledge the different meaning of the words. I would, however, be very sorry if this might lead to the idea that micro- and semimicroanalysis are methods which are at least contradictory, or to a lesser extent, have basic differences. Nothing is further from the truth; I would prefer to say that semimicroanalysis is one of the forms of microanalysis. Actually, all the basic techniques are the same; they have the same advantages and disadvantages. The semimicro method, i.e., as defined here, gravimetric analysis in which weighing is carried out to the fifth decimal place, is, in my mind, always preferable as long as the amount of material available is not so small that the "real" micromethod has to be used. In this connection, it should be remembered that, as a rule, the switch from semimicro to micro does not lead to any gain in time, since manipulation ofthe apparatus becomes more difficult, and does not lead to any appreciable economy in cost.

There are, naturally, many methods for carrying out gravimetric microanalysis, but there is one which we very often use, this is filtration through an asbestos filter and drying to constant weight at temperatures not higher than 180°, in order to avoid loss of combined water from the asbestos. Where it is necessary to dry or calcine at a higher temperature, we use filter tubes of quartz glass with a quartz filter disc, but this is usually exceptional. Instead of the well-known filter tubes with a filter of porous glass, we use either a glass tube with a drawn-out tip and a glass bead covered with asbestos, or filter sticks packed with asbestos for sucking in the inverted position. These filters are readily cleaned, and moreover, they cost next to nothing. Even now the number of reagents used forprecipitating various ions to give precipitates which can be dried to constant weight at temperatures not less than 180° (when necessary, in a vacuum) is more than sufficient, and will increase when this method has found wide application. Several years ago it was usually thought that such reagents are almost always organic reagents, but in recent years it has been shown that a large number of inorganic reagents are also suitable. In this connection the result of the thermogravimetric studies of Duval et al [2] are of interest. We are working with such methods with students in our institute, and several of the methods are being successfully used in industrial laboratories.

As mentioned above, until comparatively recently, the position with respect to titration methods was considerably less satisfactory. The old microburets had very many serious drawbacks. They were narrow tubes which were difficult to clean, while reading of the scale divisions was rendered difficult by contaminations of the walls by fatty materials. "Drainage time" was so large that calibration proved fictitious if could not be linked up with the rate at which the buret emptied. The obvious need was for small burets with small taps, but small taps always leaked. And, finally, the drops from a microburet, although actually several times smaller than the drops from an ordinary buret, did not decrease in proportion to the amount of solution, so that titration was rather inaccurate. This drawback has in recent years been successfully overcome by using burets with a long, thin, drawn-out tip which can be immersed below the liquid level; in this way drop formation is in general excluded. A few years ago elimination of two other drawbacks become possible thanks to two technical inventions; the first was the possibility of making glass tubes with a perfectly circular cross-section and of constant diameter, and the other was the use of plastics — teflon $(C_2F_4)_n$, which is not attacked by the usual titrants, while at the same time it is sufficiently stable and elastic that it is possible to make pistons which do not leak. Modern piston burets — the Swiss make Metrome with a capacity of up to 5 ml, and the German make Strohlein with a capacity of down to 0.5 ml, and maybe others of which I am unaware — have completely changed the state of affairs. Microtitration can now be carried out with scarcely greater difficulty than macrotitration by classical methods. Tap leakage has been eliminated by improving the quality of the tap, or by using large taps on small burets, which may not be very good from an aesthetic point of view, but is definitely preferable from a technical point of view.

In my opinion, microtitration will soon be in widespread use. It has the same advantages as gravimetric microanalysis with respect to economy of reagents, and is more elegant in operation; but, there is one essential difference. Microtitration is not quicker, rather it is slower than macrotitration, and requires more expensive apparatus, even if it were only the question of having to use mechanical magnetic stirrers.

All the same, even if in the near future, microburets do not supplant completely the old macroburets, I still think that the use of the latter will decrease appreciably. As experiment has shown, the micromethod often finds unexpected uses, if only to show that it cannot be used.

In general, so it seems to me, there is a basis for assuming that after a short time microanalysis will be the general method in chemical analysis — without doubt in qualitative and gravimetric quantitative analysis, and probably also in titrimetric analysis, although somewhat later. Microanalysis is an unusual, special style of work. Of course, there will always be cases where it will be better to use macro- or even supermacroanalysis, but such cases will be met less and less frequently. Industrial laboratories, in particular, cannot continue wasting time and money. True, the position is not such that one stroke of the pen will be sufficient for switching to the new method. In technical analysis there are many generally accepted methods which would give other results on altering the apparatus. For adapting them to the new style of work a large amount of work is necessary, but this is a pleasant task for closely working groups of analysts in industry.

I have fairly frequently heard the argument against microanalysis that it is not commensurate with the demands for carefully averaged (sampled) test material. I reject this argument completely. Of course, the weight of sample which should be chosen from a mass of material is determined only by the weight of the whole mass and by the degree of its homogeneity — and by nothing else. Sampling has its own rules which are completely independent of purely analytical considerations. Unfortunately, the necessity sometimes arises for using a whole liter of hydrochloric acid for dissolving the test material in order to make it homogeneous. This is sometimes unavoidable, but after homogenizing the sample, there is nothing to force us to continue wasting expensive reagents. That is the analyst's concern; if he thinks that he can carry out an analysis just as well, if not even better, by means of small laboratory apparatus, then he is justified in refusing to use a macromethod.

If everything should go precisely in this way, then it is obvious that it should be reflected in the methods of teaching analytical chemistry in our universities and special schools for training laboratory workers. In universities we usually have two different courses; in the first year the course consists of an introduction to the basis of chemistry and chemical laboratory practice, while in successive years the theoretical basis of the various methods of chemical analysis is taught. When microanalysis is touched upon, it is usually as a part of the second course together with instrumental methods of analysis, and, quite often as part of the organic chemistry course. In my opinion such a state of affairs is no longer applicable. When such a course is followed, the impression is created that there is some contradiction between microanalysis and "ordinary" analysis. It is possible to prepare introductory courses on general chemistry, without including chemical analysis, particularly analytical laboratory work; but, if we do nevertheless include it, then it should be actually done on the modern level. It is useless teaching students how their predecessors carried out qualitative and gravimetric analysis. On the other hand, if we are convinced that the micromethod is already preferable, the best way of promulgating its use in industry and research will be to teach our students this method — and nothing else — right from the first practical course. From many years experience I know that students take it up with great enthusiasm, even if it is because the better results that they obtain confirm their faith in themselves, and this is of course of primary psychological importance. They will learn later that there are still exceptions, particularly in some forms of technical analysis. At present, students are taught that the micromethod is normally used in organic analysis, but, in my opinion, the accent should be shifted radically. Maybe this will be rather sad for certain chairs of microanalysis which would cease to exist if what I suggest is put into force, but this would be their contribution to what is bound to happen in the end. By ceasing to exist as a separate entity they would demonstrate to analysts that the micro style is one of the characteristic features of the chemical analysis of tomorrow.

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ELECTRON EXCHANGING INSOLUBLE POLYMERS

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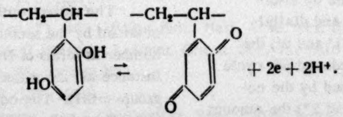
Ion exchange polymers (ion exchange resins) have found wide application in analytical chemistry, by facilitating separation of cations from anions, increasing the concentration of very dilute solutions, and replacing tedious extraction processes by filtration methods [1]. The use of ion exchange resins has led to the creation of ion exchange chromatography [2]. Nevertheless, the use of this method in many instances requires preliminary separation from the solution of some of the ions, or the conversion of some of them into other valence forms in order to give them properties which will differentiate them from other ions found in the same solution. Addition to the solution of precipitants, and of oxidizing or reducing agents, complicates the composition of the solution, often leading to an unacceptable change in the pH of the solution and in its concentration. It is better to use for these cases readily regenerated electron exchanging polymers [3, 4]. On filtering a solution through a column filled with granules of such a polymer, it is possible to lower the valence of such ions as Cu^{2+}, Fe^{3+}, Mn^{VII}, Ti^{IV} and, in this way, facilitate their separation from accompanying ions. Reduction of silver, mercury, and gold ions and oxidation of chloride, bromide, and iodide ions permits their separation from solution. Finally, by filtering a solution through electron exchanging polymers it is possible to remove oxygen dissolved in them.

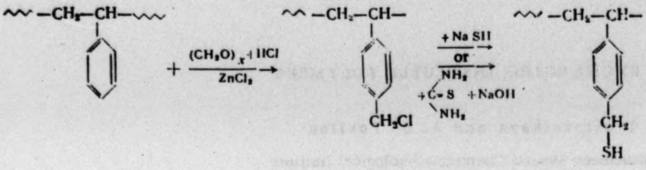
Electron exchanging polymers are synthesized by copolymerization of vinylhydroquinone with styrene or vinylpyridine or by the copolycondensation of hydroquinone and phenol with formaldehyde [5, 6]. Electron exchange is determined by the reversible transition of the hydroquinone chains of the macromolecule of the polymer into the quinoid form:



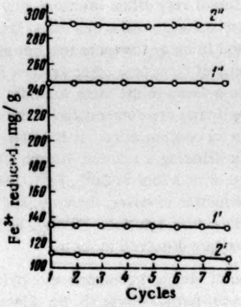
The electron exchanging polymers have not found wide practical application since they possess low mechanical strength and chemical stability. This obviously also explains the decrease in their electron exchanging capacity after several oxidation and reduction cycles.

Gregor [7] and Parrish [8] have suggested that electron exchanging polymers can be prepared by introducing sulfhydryl groups into copolymers of styrene and divinylbenzene. These authors have not given any data on the conditions used for synthesizing the thiolcopolymers, or the properties of the materials they prepared. We have checked on methods for preparing sulfhydryl copolymers, and have established the most favorable conditions for carrying out this reaction and for studying the properties of the thiolcopolymers. The starting materials we chose were chloromethylated copolymers of styrene and divinylbenzene (SD) or diallylmaleate (SAM). The copolymers were prepared by granulated copolymerization in which the granule size was 0.25 to 0.5 mm. The granules were kept in dichloroethane in order to swell them, they were then chloromethylated by the simultaneous action of

paraform and hydrogen chloride in the presence of zinc chloride. The chloromethylated polymer SD contained 14% chlorine, while the polymer SAM contained 16% chlorine. Replacement of the chlorine atoms in the copolymers by sulfhydryl groups can be realized by the action of sodium sulfide or thiourea with subsequent saponification with alkali.



In the first case the granules of the chloromethylated copolymer was allowed to swell in dioxane and then mixed with an alcoholic solution of sodium sulfide; the mixture was heated at 90-95° for 10 hours while being stirred. After extracting the granules and then regenerating with a hydrochloric acid solution, it was found that the sulfur content was 2.45%, while the acid number in terms of NaOH was 30 mg/g. Accordingly, the copolymer contained sulfur only in the form of sulfhydryl groups (–SH). On passing a $FeCl_3$ solution through a column packed with granules of this type at the rate of 3 ml/min, it was possible to reduce 156.8 mg of Fe^{3+} to Fe^{2+} per g of copolymer. Of this 44.8 mg/g of Fe was absorbed by the copolymer. The absorbed iron ions were eluted with a strictly equivalent amount of hydrogen ions.

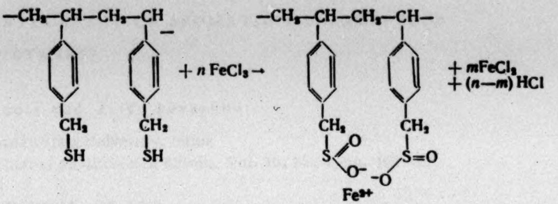


Reduction of Fe^{3+} ions by thiolcopolymers of styrene and divinylbenzene (1' and 1") and by thiolcopolymers of styrene and diallylmaleate (2' and 2"). 1' and 2') the amount of Fe^{3+} ions reduced per cycle and the amount absorbed by the copolymer, mg/g; 1" and 2") the amount of Fe^{3+} ions reduced after the same cycles, but carried out in the filtrate, mg/g.

It was found possible to introduce a considerably greater amount of sulfhydryl groups into the copolymer by interacting it with thiourea. For this purpose the granules of the chloromethylated copolymer which had been allowed to swell in dioxane were mixed with a solution of thiourea mixed with dioxane and alcohol. The reaction was carried out for six hours on heating and stirring at 90-95°. The granules, which did not alter their external appearance, were saponified with an alcoholic solution of alkali and converted into the acid form by means of a hydrochloric acid solution.

The sulfur content of the sulfhydryl copolymers obtained by the second method was 11% while the acid number in terms of NaOH was 156 mg/g. In the given instance all the sulfur in the copolymer formed thio groups (–SH). The copolymer swelled slightly in water (18-20%), while maintaining its glass-like appearance and the high stability characteristic of the original copolymers. The reducing capacity of the thiolcopolymers, and the reproducibility of this capacity after eluting the absorbed ions and restoring the polymer (regeneration), were checked by the dynamic method. Regeneration of the polymer was effected by washing it with a 10% sodium hydrosulfite solution, the volume of the latter used being 15 times the volume of the column occupied by the thiolcopolymer. The results of these experiments are given in the Figure. The complete reducing capacity of the sulfhydryl copolymer SD with respect to iron ions was 380.8 mg/g; while for the copolymer SAM the value was 392 mg/g. Of this amount of iron, 134 mg of iron was absorbed by the polymer and was eluted by the acid solution. After elution of the iron ions, the polymer, prior to its regeneration, with sodium hydrosulfite, was deprived of its capacity to reduce ions, but preserved the properties of an insoluble weak acid and was capable of exchanging hydrogen ions for cations. Its acid number in terms of NaOH was 116 mg/g. Accordingly, during the process of reducing iron ions, 75% of the sulfhydryl groups are oxidized to a new acid form, which preserves the capacity of the copolymer to exchange cations. The new acid groups, however, have a low degree of ionization. At a pH greater than 10 the capacity with respect to sodium ions amounted to 2.9 meq/g, which dropped to 1.8 meq/g at pH 7, while its capacity with respect to iron ions in a $FeCl_3$ solution was 0.4 meq/g.

Probably, the greater part of the sulfhydryl groups of the copolymer are oxidized to form sulfinate groups, which enter into an ion exchange reaction with part of the reduced cations:



The sulfhydryl copolymers reduced 80 mg/g cupric ions from a $CuCl_2$ solution to cuprous ions, 22 mg/g of this amount being absorbed by the copolymer. By means of the thiolcopolymers it was found possible to reduce 150 mg/g of silver ions to metallic silver.

SUMMARY

Conditions have been established for preparing electron exchanging copolymers containing sulfhydryl groups.

It has been shown that these thiolcopolymers have a high electron exchange capacity, which does not change in the course of 8-10 oxidation—reduction cycles.

It has been established that the electron exchange process is accompanied by an ion exchange. This gives a basis for suggesting that the reversible oxidation of the sulfhydryl groups of the copolymer occurs prior to the formation of sulfinic acid chains.

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PARTITION CHROMATOGRAPHY OF AROMATIC HYDROCARBONS ON RUBBER-LIKE POLYMERS*

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At present partition chromatography is one of the most important methods of chromatographic analysis [1]. Until recently hydrophilic carriers have been used exclusively as the stationary phase in partition chromatography. Accordingly, the overwhelming majority of organic materials, including hydrocarbons of all classes, could not be used as test materials for this method. Recently [2, 3] attempts have been made to overcome this difficulty by introducing hydrophobic carriers, raw and vulcanized rubber having been suggested for this purpose. By using benzene and n-heptane as the stationary phases it has been found possible to separate some mixtures of polar organic materials (fatty acids, nitrotoluene, etc). Further, in partition chromatography one must always take into account the danger of superposition of the adsorption isotherm on the partition isotherm, since it is difficult to find a carrier the adsorption properties of which can be completely ignored.

Accordingly the idea of the possibility of doing without a carrier in partition chromatography is very attractive. At first glance such an idea would seem to be out of the question, however, recently [4] the possibility was suggested of using high polymers not only as a carrier but directly as the stationary phase.

The possibility of using rubber-like high polymers in partition chromatography as the stationary phase was given its first experimental foundation in [5]; in these papers a detailed study was made of the partition of hydrocarbons between the high polymer phase and the phase of the low molecular weight organic liquids. It was shown that rubber-like high polymers are selective solvents for hydrocarbons, while equilibrium partitioning is established fairly rapidly, particularly when weakly linked and unfilled high polymers are used.

In the work described here, the chromatographic method based on the partitioning of the test components between the stationary high polymer phase and the mobile low molecular weight liquid, has been used for the separation of aromatic hydrocarbons.

EXPERIMENTAL

The stationary phase used was a SKB vulcanizate of the following composition: SKB, 100 parts by weight; sulfur, 2 parts by weight; ruberax, 3 parts by weight; captax 1.25 parts by weight; stearic acid, 1.25 parts by weight; diphenylguanidine, 0.5 part by weight; and zinc oxide, 5 parts by weight.

Sheets of the rubber approximately 1 mm thick were cut into small pieces which were ground in an agate mortar into a powder with an average particle size of 0.30 mm, after preliminary swelling in benzene. The powder obtained was carefully washed with benzene, a mixture of benzene and methanol in the proportion of 1 : 1, and finally with methanol, these solvents being changed daily until the refractive index of the solvents was the same as that of the original solvents.

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* Delivered at the analytical section of the VIII Mendeleev Conference March 21, 1959.

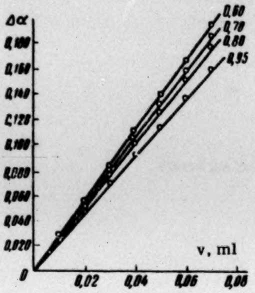

Fig. 1. Δα) The increase in the yield angle; v) no. of ml of hydrocarbon in 50 ml of solution.

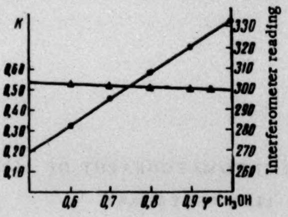

Fig. 2. K) Angular coefficient (slope); φ) volume fraction of methanol; ▲) curve for slopes; ●) calibration curve of the interferometer.

Mixtures of methanol and water containing 37.2, 36.3, 29.4 and 24.6 percent by volume of water were used as the mobile phase. The choice of mixtures with such composition was made on the basis of a preliminary study of the partition coefficients of aromatic hydrocarbons between the polymer and the methanol–water mixtures of varying composition. The partition coefficients were calculated as the ratio of the solubility of the corresponding hydrocarbon in the polymer phase and in the binary solution phase. The solubility of the hydrocarbon in the polymer was determined from results on the swelling of carefully washed sheets with time, the true value of the swelling being found by the usually accepted method [6], by extrapolating the curves for the kinetics of swelling to zero time. The extrapolated swelling values were used for calculating the solubility of the corresponding hydrocarbon in the polymer (g/cm^3), since the specific volume of the washed polymer (equal to 0.998 cm^3/g) had been established. The solubility of the hydrocarbons in the mobile solvents was determined in the usual way. Experiments to determine the solubility were carried out in an air thermostat at a temperature of 23 ± 0.5°.

The results obtained for the solubility of the hydrocarbons in both phases, as well as the partition coefficients calculated by means of these results (expressed in g/cm^3) are given in Table 1 for all the mobile solvents used in the present work for separating mixtures of aromatic hydrocarbons.

TABLE 1

No.	Water content of the mobile phase, %	Hydrocarbon	Solubility in the mobile solvent, g/cm^3	Solubility in the stationary solvent, g/cm^3	K
		Benzene	0.413	0.802	1.94
1	37.2	Toluene	0.191	0.723	3.78
		Toluene	0.225	0.723	3.21
2	36.3	para-Xylene	0.069	0.711	10.30
3	29.4	para-Xylene	0.301	0.711	2.36
		Mesitylene	0.102	0.712	7.00
		Mesitylene	0.177	0.712	4.02
4	24.6	n-Hexane	0.088	0.470	5.60

It is known that [1] the separation of two materials by partition chromatography is more effective, the greater the difference in their partition coefficients.

It is evident from Table 1, that the mobile solvents we have chosen, in the order in which their numbers increase, are fully suitable for separating benzene, toluene, p-xylene, and mesitylene from their mixtures. It is also clear from the Table that solvent No. 4 can be used for separating mesitylene from n-hexane.

Construction of the yield (elution) curve is bound up with the analysis of a three-component system:

TABLE 2

Hydrocarbon	R	$K_{calculated}$	$K_{experimental}$
Benzene	0.8	2.1	1.9
Toluene	0.49	3.9	3.5
p-Xylene	0.39	5.5	–
Mesitylene	0.34	6.4	–

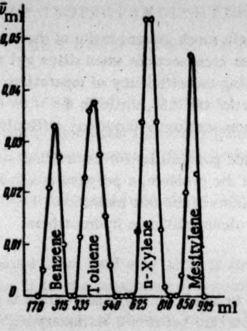

Fig. 3. $\bar{V}$) No. of ml of hydrocarbon; V) no. of ml of mobile solvent.

methanol–water–hydrocarbon. The following technique was developed for analyzing ternary systems.

Using a IRF-23 refractometer, calibration curves were contructed relating increase in refractive index with hydrocarbon concentration for a number of ternary mixtures with a fixed amount of alcohol by volume. These curves (Fig. 1) for the system methanol–water–toluene are straight lines issuing from the origin, the slope of the lines being dependent on the parts by volume of alcohol in the ternary system. Calibration curves were were also constructed in which the slope of the straight lines was plotted against the parts by volume of alcohol. The latter were measured on a Zeiss liquid interferometer using a calibration curve constructed beforehand of refractive index against the parts by volume of methanol in twice-distilled water saturated with the corresponding hydrocarbon. All the calibration curves (Fig. 2) were constructed for a temperature of 22±0.5°.*

The number of ml of test hydrocarbon in the collector was determined as follows: 1 ml of the test solution was transferred to a 200 ml standard flask and made up to the mark with twice-distilled water. Three ml of the solution obtained and 1-2 drops of the hydrocarbon were placed in the interferometer chamber, and, after shaking in order to obtain constant readings, the readings of the interferometer were taken. Using the calibration curves (see Fig. 2) the parts by volume of alcohol in the test solution was determined, as well as the slope of the curve relating refractive index to hydrocarbon concentration for the solution whose content of alcohol in parts by volume has been found; the refractive index of the test solution was also measured. The number of ml of hydrocarbon in 50 ml of the test solution was calculated by means of the formula** $V = \Delta\alpha / K$ where $\Delta\alpha$ is the increase in the yield angle with respect to the binary mixture with the same content of alcohol in parts by volume, as is contained in the test solution, while K is the slope of the curve. Since, in fact, the volume of the solution was always less than 50 ml, the result obtained was correspondingly decreased, and this led to a decrease in the experimental error.

The chromatographic experiments were carried out in a column 1.60 cm in diameter, the height of the stationary phase being 26.4 cm. Since the specific gravity of the polymer was 1.002 g/cm^3, the cross sections of the stationary and mobile solvents were 0.72 and 1.29 cm^2, respectively. Before introducing the test mixture, part of the mobile solvent was let out of the column and the test mixture introduced directly into the upper part of the stationary phase. After allowing to soak in for 1-2 hours, the mobile solvent was passed through the column at the rate of 0.2 ml/min. The volumes of the collectors range from 5 to 25 ml.

In Fig. 3 are shown typical elution curves for one of the experiments in which a mixture consisting of 0.100 ml of benzene, 0.150 ml of toluene, 0.200 ml of p-xylene, and 0.100 ml of mesitylene was separated. The amounts of these hydrocarbons actually found were 0.105 ml, 0.155 ml, 0.210 ml, and 0.100 ml, respectively.

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*The numbers of the straight lines in Fig. 2 denote the parts by volume of methanol in the original binary solution.

**The calibration curves relating refractive index to concentration were constructed for 50 ml of solution.

The average experimental error does not exceed 5%.

It is clear from Fig. 3. that the partition coefficients of the hydrocarbons differ so much for the mobile solvents chosen that separation of the hydrocarbons can be accomplished without any danger of obtaining mixed zones.

Table 2 contains the values for the mobility of the hydrocarbons, and also the partition coefficients calculated by means of them for benzene and tolune. The latter coincide satisfactorily with the experimentally determined values of the partition coefficient for benzene and toluene, since the compositions of the mobile solvents were similar for these hydrocarbons. As for p-xylene and mesitylene, the zone of the first is displaced by three, and the zone of the second is displaced by the four mobile solvents. Accordingly, a similar comparison is impossible for p-xylene and mesitylene.

The use of high polymers as the stationary phase allows one to obtain much greater ratios of the cross sections of the stationary to the mobile phase, as compared with the ratios of these cross sections when silica gel and other carriers are used as the carrier; this is of essential importance for increasing the efficiency of separation. Thus, in the work of Martin and Synge on the separation of amino acids [7] this ratio was 0.35, while in the work described here it is 0.56, so that it is possible to get much more favorable phase cross sections without any difficulty.

Polymerization, and, in particular, copolymerization opens up wide possibilities for controlling the properties of stationary phases. Accordingly, depending on the conditions of the problem, a polymer or copolymer can can be chosen which will ensure optimum values for the partition coefficients of the test materials. The variant suggested, presumably, may be of special interest for the analysis of petroleum distillate hydrocarbons.

SUMMARY

A new variant of the chromatographic method has been developed in which the stationary phase is used without a carrier; it is based on partitioning of the components to be separated between a stationary high molecular weight phase and a low molecular weight phase.

It has been shown that by using unfilled SKB vulcanizate containing 2% of sulfur as the stationary phase, and methanol–water mixtures as the mobile phase, it is possible to get a clear-cut separation of a mixture of aromatic hydrocarbons, and also to separate aromatic hydrocarbons from aliphatic hydrocarbons.

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THE RELATION BETWEEN R_F VALUES AND THE COMPOSITION OF ISOPROPANOL–HYDROCHLORIC ACID (1:1) MIXTURES USED AS ELUANT

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Isopropanol is not used very much in inorganic chromatography although satisfactory results have been obtained on using it for the separation of a number of elements [1-4].

A systematic study of changes in R_F values with HCl concentration has enabled us to make some general conclusions regarding the possibility of using the R_F values for various separations in practice. The conclusions which we have formulated are in fairly good agreement with the results of G. de Carvalho [5] for the eluant butanol–hydrochloric acid.

EXPERIMENTAL

Ascending chromatography on Whatman paper No. 1 was used. Ten mixtures of eluant were prepared for each series of experiments; they were: 250 ml of isopropanol and 250 ml of HCl 1 N, 2 N, 4 N, 5.5 N, 6 N, 7 N, 8 N, 9 N, 10 N, and 12 N. These mixtures were kept overnight in the chromatographic tanks in order to saturate the air in the latter.

TABLE 1

Developer	Ions	Developer	Ions
Sodium cobaltinitrite	K, Rb, Cs	Ammonium sulfide	Pb, Bi
Zinc uranyl acetate	Na, Li.	Potassium iodide	Tl
Ammoniacal solution of 8-hydroxyquinoline	Sc, Y, La, Th, Sn	Nessler's reagent	NH_4^+
Alizarin S	Be, Mg, Ca, In, Al, Zr	Dithizone	Zn, As, Sb
Sodium rhodizonate	Sr, Ba	Chugaev's reagent	Ni
Ammonium thiocyanate followed by $SnCl_2$	Mo, W	Diphenylcarbazone	Cd, Hg, Co.
Tin chloride	Se, Te	Potassium ferrocyanide	Cu, U, F

A drop of solution to give a spot 0.6 cm in diameter was placed by means of capillary pipet at a distance of 1 cm from the lower edge of the chromatographic paper 24 x 1.5 cm. In most cases 0.1 N solutions of the chlorides in HCl were used.

A large number of elements were chromatographed by the method indicated. After drying for 30 minutes in air the paper was placed in the tank containing eluant of the concentrations indicated above and kept there for

TABLE 2

Ions \ HCl *N*	1	2	4	5,5	6	7	8	9	10	12
NH_4^+	0,10	0,12	0,27	0,52	0,49	0,49	0,48	0,47	0,46	0,42
Li^+	0,10	0,13	0,27	0,52	0,50	0,48	0,47	0,46	0,45	0,42
Na^+	0,06	0,08	0,27	0,41	0,40	0,39	0,37	0,34	0,27	0,22
K^+	0,03	0,04	0,18	0,36	0,36	0,34	0,33	0,30	0,23	0,17
Rb^+	0,04	0,05	0,21	0,43	0,40	0,40	0,40	0,35	0,33	0,27
Cs^+	0,04	0,05	0,24	0,48	0,46	0,46	0,45	0,37	0,39	0,38
Cu^{2+}	0,10	0,12	0,30	0,46	0,51	0,55	0,58	0,58	0,58	0,57
Ag^+	0	0	0	0	0	0	0	0	0	0
Be^{2+}	0,14	0,20	0,46	0,64	0,64	0,65	0,66	0,68	0,70	0,72
Mg^{2+}	0,05	0,15	0,30	0,53	0,53	0,55	0,56	0,55	0,55	0,44
Ca^{2+}	0,02	0,14	0,28	0,43	0,43	0,47	0,48	0,47	0,47	0,45
Sr^{2+}	0,02	0,12	0,25	0,37	0,37	0,41	0,46	0,34	0,34	0,34
Ba^{2+}	0	0,11	0,19	0,27	0,27	0,30	0,33	0,23	0,23	0,22
Zn^{2+}	0,58	0,78	0,95	1,00	1,00	0,93	0,89	0,84	0,81	0,76
Cd^{2+}	0,50	0,70	0,91	1,00	1,00	0,97	0,96	0,95	0,90	0,80
Hg^{2+}	0,80	0,85	1,00	1,00	1,00	1,00	1,00	0,98	0,91	0,86
Al^{3+}	0	0,02	0,20	0,42	0,40	0,38	0,37	0,35	0,34	0,26
In^{3+}	0,24	0,28	0,73	0,77	0,76	0,68	0,55	0,50	0,47	0,46
Tl^{3+}	0,82	0,99	1,00	1,00	1,00	0,99	0,99	0,99	0,98	0,96
Sc^{3+}	0	0,02	0,16	—	0,29	—	0,28	—	0,27	0,20
Y^{3+}	0	0	0,16	—	0,27	—	0,26	—	0,25	0,18
La^{3+}	0	0	0,15	—	0,27	—	0,26	—	0,26	0,17
Ti^{IV}	0,04	0,08	0,28	—	0,45	—	0,42	—	0,40	0,42
Zr^{IV}	0	0	0,10	0,26	0,24	0,23	0,23	0,20	0,16	0,12
Th^{4+}	0	0	0,16	0,38	0,35	0,20	0,19	0,18	0,16	0,12
Ge^{IV}	0,25	0,32	0,60	0,85	0,85	0,89	0,95	0,97	0,97	0,99
Sn^{IV}	0,67	0,79	0,95	0,95	0,97	0,97	0,97	0,97	0,96	0,95
Pb^{IV}	0,11	0,17	0,39	0,58	0,55	0,54	0,52	0,49	0,46	0,37
As^{III}	0,40	0,48	0,56	—	0,68	—	0,89	—	0,84	0,77
As^{V}	0,40	0,49	0,59	0,68	0,70	0,84	0,97	0,96	0,95	0,83
Sb^{V}	0,60	0,70	0,90	1,00	1,00	1,00	0,91	0,88	0,83	0,74
Bi^{V}	0,32	0,40	0,60	0,83	0,81	0,76	0,72	0,65	0,63	0,58
Cr^{VI}	0,30	0,38	0,56	0,77	0,75	—	0,72	—	0,59	0,58
Mo^{VI}	0,14	0,20	0,37	—	0,50	—	0,51	—	0,56	0,58
W^{VI}	0	0	0	—	0	—	0	—	0	0
U^{VI}	0	0	0,30	0,52	0,49	0,46	0,46	0,46	0,46	0,43
Se^{VI}	0,50	0,68	0,83	0,83	0,83	0,88	0,95	0,96	0,97	0,99
Te^{VI}	0,63	0,78	0,89	0,93	0,93	0,93	0,93	0,95	0,96	0,98
Fe^{2+}	0,11	0,18	0,32	—	0,54	—	0,79	—	0,95	1,00
Fe^{3+}	0,45	0,63	0,80	0,91	0,94	0,96	0,97	0,98	1,00	1,00
Ni^{2+}	0	0,03	0,20	0,42	0,40	0,38	0,37	0,36	0,42	0,63
Co^{2+}	0	0,03	0,22	0,40	0,39	0,38	0,38	0,35	0,29	0,25

TABLE 3

HCl concentration of the eluant, N	Ferric chloride content in 2 ml, g	
	Aqueous phase	Alcoholic phase
2	0.49	0.24
4	0.60	0.25
5.5	0.65	0.36
6	1.04	0.58
8	1.33	—

TABLE 4

HCl concentration in the eluant, N	Solubility of NaCl per ml	Solubility of $AlCl_3$ per ml
1	0.53	—
2	0.18	0.33
4	0.046	0.32
5.5	0.030	0.31
6	0.020	0.31
8	0.016	0.30

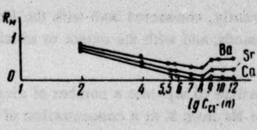

Fig. 1

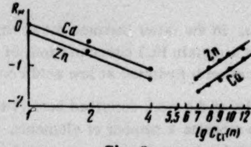

Fig. 2

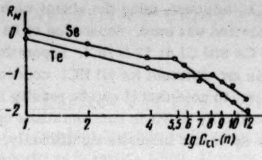

Fig. 3

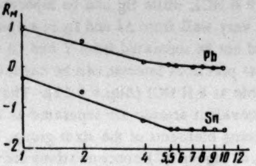

Fig. 4

12 hours until the solvent front had advanced 23 cm. The paper was then dried again and the spots developed with the appropriate reagents (Table 1). The temperature was kept constant at 22.5±0.5° during the runs.

The distance from the center of the developed spot to the starting line was measured in order to determine the R_F value.

From an examination of the R_F values as a function of the hydrochloric acid concentration, it follows that for all the ions tested, as in the analogous studies of Carvalho [5] with butanol–hydrochloric acid, the maximum R_F values are obtained for the majority of the elements at a concentration of about 5.5 N (Table 2).

The behavior of the various ions is determined by the increase in solubility of the simple chlorides and the chloro complexes formed. This occurs, for example, in the case of Cu, Fe, and Mo ions for which there is observed an increase in the R_F value along the whole concentration range of HCl used. As Lederer [6] has pointed out, the R_F values increase with increasing formation of chloro complexes which are ionized to a lesser extent and are more soluble in organic solvents. In order to confirm this assumption we prepared saturated solutions of $FeCl_3$ (about 12 g) in 25 ml flasks for a series of mixtures of isopropanol and 2 N, 4 N, 5.5 N, 6 N, and 8 N HCl; they were prepared at a temperature of 25° which was kept constant by means of a thermostat. Two ml of the clear saturated solution was taken from each flask and transferred to tared beakers and the solutions evaporated to dryness under vacuum. By weighing the beakers with the residues we obtained the results given in Table 3. We should point out that during the preparation of the saturated solutions of $FeCl_3$, formation of two phases was observed; moreover, on the chromatograms for Fe^{3+} double spots were obtained, probably as a result of partial reduction of Fe^{3+} to Fe^{2+} on the paper.

The solubility of copper salts also increases with increasing hydrochloric acid concentration.

An increase in the R_F values with increasing HCl concentration was also observed for Be, Ge, Se, and Te, there being a tendency to the formation of a plateau at a concentration of about 5.5 N. Similar results have been obtained by Kertes [7] for complex chloroacetonates, and by Lederer [8] for complex chlorides when acetone–HCl was used as the eluant. A linear relation between the R_F value and the negative logarithm of the concentration of the bound acid was also observed in our case. It should be noted that when the cations form complexes with similar chemical properties almost parallel straight lines are obtained. This is true for example for Ca, Sr, Ba (Fig. 1), Zn, Cd (Fig. 2), Se, Te (Fig. 3), and Pb, Sn (Fig. 4).

The solubility of the alkali metal chlorides precludes obtaining maximum R_F values at a concentration of 5.5 N, since their solubility decreases with acid concentration; the alkali metals are present in a hydrated state and are not capable of forming soluble complex chlorides (Table 4).

This lack of correspondence between the R_F values and solubility, of course, is fully possible for other elements as well which have maximum R_F values at a concentration of 5.5 N. Aluminum chloride (Table 4) is an example of this. In the latter instance the change in solubility is, apparently, connected both with the formation, starting at a certain HCl concentration, of ionized complex compounds, and with the extent to which the corresponding cation is hydrated at low acid concentrations.

The results of the work described here (Table 2) show that it is possible to separate a number of elements. It is possible to separate a number of elements. It is possible to separate Na from K at a concentration of 4 N HCl (ΔR_F = 0.09) by descending chromatography. Rb and Cs ions will also be separated well at 12 N HCl.

The elements of the second main group are separated very well at 10 N HCl. Separation of Zn and Cd can be effected at 9 N HCl, while Hg can be separated from these other two elements at low acid concentrations. Tl is separated very well from Al and In at a concentration of 5.5 N HCl; however, using the eluant we have chosen Sc could not be separated from Y and La whichever HCl concentration was used. Separation of Be and Al, which is of great practical interest, can be carried out at 10 N HCl, and Ca and Cl at 12 N HCl. Separation of Zn and Th is possible at 6 N HCl (ΔR_F = 0.11). The R_F values for Ge and Sn are different for all HCl concentrations. Tri- and quinquevalent arsenic are separated at 10 N HCl. It is of interest to note that U can be readily separated from the remaining elements of the sixth group, although it behaves identically to Th in concentrations up to 4 N HCl; however, at higher HCl concentrations the difference between the R_F values increases significantly; U, Th, and Zr are best separated at 5.5 N HCl.

Ni and Co ions are readily separated at 10 N HCl.

It should be observed that in absorption chromatography, separation on the basis of the formation of complexes is particularly successful. The results of the work by Gurvich and Gapon [9] and Shemyakin and Mishchelovskii [10] are very illuminating in this respect.

SUMMARY

A study has been made of the relation between R_F values and HCl concentration in isopropanol−HCl mixtures (1 : 1) used as eluant.

The results obtained generally agree with those of G. de Carvalho who used butanol−HCl (1 : 1) as eluant.

There is some correspondence between the solubility of the chlorides or chloro complexes and the R_F values obtained. It has been shown that it is possible to separate a large number of elements.

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REASONS FOR THE ENHANCED PRECISION OF SPECTROGRAPHIC ANALYSIS ON USING AN IMPULSE EXCITATION SOURCE

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In previous articles [1, 2] the expediency has been demonstrated of using an impulse excitation source for increasing the precision of spectrographic analysis, and, by means of radioactive isotopes the first information on the spatial distribution of atoms in the interelectrode gap of this source was obtained. The present article is devoted to the continuation of these researches. The aim of this work was a more systematic study of the most important physical parameters of the impulse arc which can affect the precision of a determination; it was also aimed at clarifying the reasons why the precision which can be attained on using this source is greater than that possible when an ordinary dc or ac arc is used. The temperature of the source was measured more accurately, the current strength in the impulse was evaluated, and additional experimental data was obtained on the mechanism of the passage of test materials into the discharge zone.

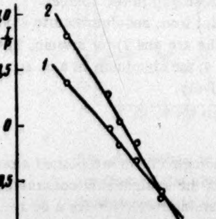

Fig. 1. Determination of the temperature of the source by Ornstein's method. 1) Impulse arc; 2) dc arc.

Determination of the Temperature of the Source and of the Current in the Impulse. The temperature of the impulse source was determined by means of Ornstein's method on the basis of the BiI lines. The wavelengths of the bismuth lines used, as well as the values of the higher energy levels (E_{ik}) and the probabilities of the corresponding transitions (P_{ik}) necessary for calculating the temperature are given in [3].

For comparison, the temperature of an ordinary dc arc was measured at the same time as that of the impulse source, using the same lines. Zinc oxide was used as the filler in both cases. The temperature of a dc arc with this filler has been measured several times already, and this facilitated comparison of our measurements with published figures [3, 4]. Bismuth was introduced into the arc anode in the form of a mixture of ZnO and Bi_2O_3, the amount of the latter being 0.3%, at this level according to the results in [3] one does not have to take into account the effect of reabsorption on the results of the determination of temperature. The relative intensity of the lines was measured by the usual method. In Fig. 1 are given the results of one series of experiments on the measurement of the temperature of an impulse arc and of a dc arc. The energies of the upper levels of the corresponding Bi lines in cm^{-1} are plotted

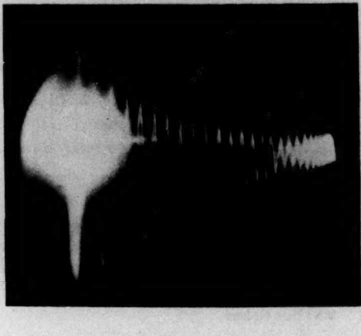

Fig. 2. Oscillogram of the current of a dc impulse arc.

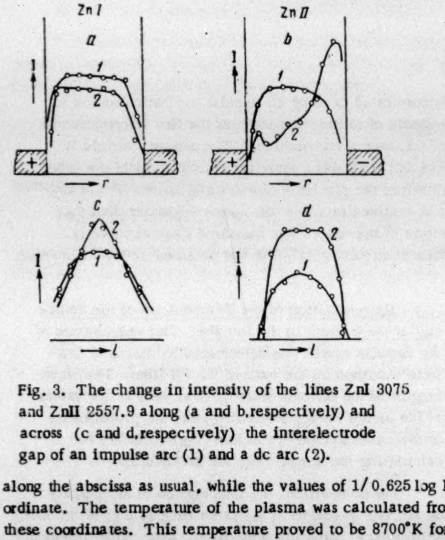

Fig. 3. The change in intensity of the lines ZnI 3075 and ZnII 2557.9 along (a and b, respectively) and across (c and d, respectively) the interelectrode gap of an impulse arc (1) and a dc arc (2).

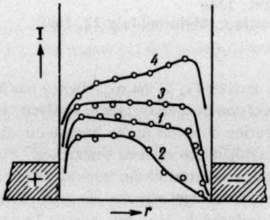

Fig. 4. Change in the intensity of the lines of excited neutral atoms of various elements along the interelectrode gap in two sources: 1) For arsenic, iron, and aluminum in a dc impulse arc and 2) for arsenic, 3) for iron, 4) for aluminum in a dc arc, respectively.

along the abscissa as usual, while the values of $1/0.625 \log I/P$ corresponding to them are plotted along the ordinate. The temperature of the plasma was calculated from the slope of the straight line constructed within these coordinates. This temperature proved to be 8700°K for an impulse arc and 6200°K* for a dc arc. The latter value coincides in accuracy with data obtained earlier in the work of Ornstein, Brinkman, and Sobolev. The higher temperature of the impulse arc is obviously connected [5, 6] with the higher current density in this source as compared with the ordinary arc. In order to evaluate the current strength in the impulse we made use of the simplest variant of an oscillographic scheme [7, 8] with a slave sweep, the advantage of which is that it starts synchronously each time with the beginning of the phenomenon being studied, and is independent of the periodicity of the process being studied. Using a slave sweep as shown earlier [7] it is possible to photograph the oscillogram with the requisite exposure, since the process under investigation is repeated with great accuracy on the oscillograph screen. In

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* These temperatures which are determined on the basis of the comparatively readily excited BiI lines, characterize, presumably, the temperature of the peripheral region of the gas cloud of the source. We did not examine the problem of the temperature of the central region of the plasma, in which (for example, in the spark), according to results obtained in recent years [10], higher temperatures can be observed.

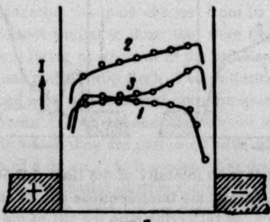

Fig. 5. Change in the intensity of the line NaI 5895.9 along the interelectrode gap of various sources. 1) ac impulse arc; 2) dc impulse arc; 3) dc arc.

order to obtain oscillograms of the current in an impulse source, a copper rod was set up at a distance of several centimeters from the interelectrode gap, by means of this rod an induced impulse was fed to the input of a ÉO-53 oscillograph. The latter was provided with an amplifier with a frequency transmission band covering 2 to 10 Mc/sec and a marking generator with a period of 1 μ sec. The fairly stable picture of the impulse obtained on the screen was photographed by means of "Zenith" photographic apparatus using a "fluorographic" plate with a sensitivity of 900 GOST units. One of the oscillograms obtained in this way is shown in Fig. 2. By means of the marking generator and the oscillogram it was possible to determine the duration of an impulse and to calculate the induction of the oscillating circuit and the input wires. The first of these was found to be $1.4 \cdot 10^{-5}$ sec, while the second was $0.44 \cdot 10^{-6}$ H. Knowing these values and taking into account the number of discharges of the condenser in the half period of the current (five discharges), it is possible by means of the formula $I_{max} = V_{max}\sqrt{C/L}$ to obtain an approximate value for the maximum current in the impulse. In our case this proved to be 540 amp, which is in reasonably good agreement with theoretical evaluations we had carried out earlier of this value [6]. It should be noted that the current strength we have determined, and the source temperature corresponding to it, are maximum values, since a further increase in current strength leads to an appreciable extension of the plasma, and, accordingly to a decrease in current density [5].

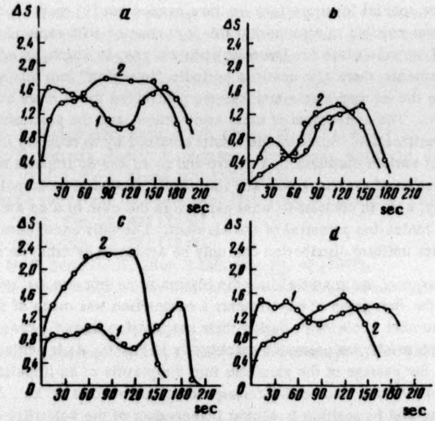

Fig. 6. Change in blackening difference ($S_{line} - S_{background}$) for lines of the elements with time, during their evaporation from a crater in the carbon electrode in an impulse arc (1) and in a dc arc (2). a) For silicon; b) for titanium; c) for aluminum; d) for iron. The relative position of curves (1) and (2) on the diagrams is arbitrary.

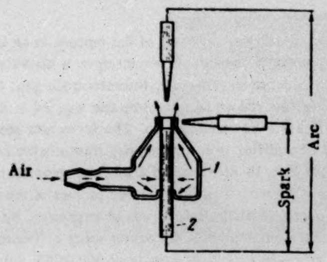

Fig. 7. Schematic diagram of the experiments used in studying the effect of the spark jet on the spatial distribution of excited zinc atoms and ions.

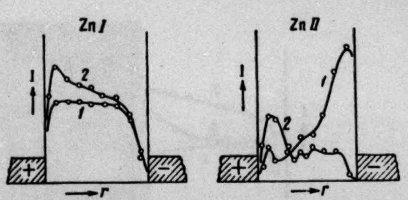

Fig. 8. Change in intensity of the lines ZnI 3075 and ZnII 2557.9 along the interelectrode gap of an impulse source, on reflecting onto the slit of the spectrograph the radiation from the channel of a dc arc in the absence (1) and in the presence of (2) a spark jet.

Spectrographic Investigation of the Mechanism of the Passage of Materials into the Interelectrode Gap of an Impulse Arc and the Spatial Distribution of Atoms and Ions in this Arc. It is known [1] that the use of an impulse arc significantly enhances the precision of the spectrographic determination of the main components of silicates. On the basis of the results of some special investigations we have carried out [2] on the spatial distribution of atoms and ions in this source it was possible to assume that this is connected with some characteristic features of the mechanism of the passage of materials into the interelectrode arc gap, in which, in addition to the ordinary fractional evaporation of the elements, there also occurs a periodic "injection" into this space of the molten mass of test sample; at the same time the excited atoms and ions are distributed much more uniformly in the impulse source than in the ordinary dc arc. The correctness of these assumptions, and the preliminary conclusions, however, required further experimental verification. Some of the results obtained by us recently in experiments on the study of the spatial distribution of various elements in a dc arc and in ac and dc impulse arcs are shown in Figs. 3, 4, 5. As is evident, the distribution of excited atoms and ions in the plasma of an impulse arc does in fact differ in its significant uniformity, and, in contrast to what happens in the case of a dc arc, the intensity (I) in most cases is independent of the ionization potential of the element. The only exceptions are elements with low ionization potentials; in such cases uniform distribution can only be achieved by using an ac impulse arc.

The mechanism of the passage of test material into the plasma of an impulse arc was studied in two series of independent experiments. In the first group of experiments a comparison was made of the curves for the change in blackening of like lines of a number of elements during their evaporation from the crater in the carbon electrode of two sources. Some of the results are presented graphically in Fig. 6. As is evident, on all the curves characterizing the conditions for the passage of the elements into the plasma of an impulse source, there is observed an additional maximum to that observed on the corresponding curves for a dc arc; this maximum appertains to the initial period of arc burning and its position is almost independent of the volatility of the test element and changes in the composition of the base. We checked this latter fact experimentally taking as examples the evaporation of a number of elements from silicate and carbonate rocks. It seems quite justifiable to explain the occurrence of the additional maximum on the curves of Fig. 6 by the "injection" mechanism suggested earlier [2] according to which part of the molten rock is injected into the interelectrode gap of the impulse source.*

In the first period, when the sample being evaporated is found close to the electrode surface, this effect shows up particularly clearly. Subsequently, as the effective depth of the opening in the electrode increases, as a result of differences in the rates of evaporation of test sample and burning of the carbon electrode, the part played by fractional distillation increases.

Conclusions as to the essential change which occurs in the mechanism of the passage of test material into the plasma of the source on switching over from a dc arc to an impulse arc can also be made by analyzing the results of the second group of experiments, in which an attempt was made to study the distortion introduced into the picture of the spatial distribution of atoms and ions in the plasma of a dc arc under the influence of a spark jet. For separating the spark channel from its jet, experiments were carried out using a scheme shown in Fig. 7, under conditions similar to those that were first suggested for this purpose in [9]. In order to prevent the quartz tube [1] from fusing on account of the arc discharge, it was cooled with a weak current of air. The lower carbon electrode was packed with ZnO. The radiation of the spark discharge together with the radiation from the jet superimposed on it was reflected onto the spectrograph slit. The photographs obtained of the spectra of the gaps were photometrically measured with respect to the arc and spark lines of zinc. The experimental results are given in Fig. 8, in which they are compared with curves illustrating the spatial distribution of excited atoms and ions in the plasma of a dc arc. It is evident that the presence of spark jet in the dc arc basically modifies the shape of the curves for the spatial distribution of excited atoms (and particularly ions) in the plasma, and always leads to the appearance of a radiation maximum in the region of the interelectrode gap near the anode. At the same time, it is clear that in order to give a correct explanation of the reasons for the uniform distribution of excited atoms and ions in the plasma of an impulse arc, it is impossible not to take into account the decisive influence exerted on this distribution by processes which occur in the spark channel of the impulse source.

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* When this series of experiments was carried out it was observed that the influence of effects connected with the "injection" of test material into the plasma of the source, increases even more on switching over to an ac impulse arc.

SUMMARY

A number of the most important physical parameters of dc and ac impulse arcs has been studied. The temperature of the arc was found to be 8700°K, while the maximum current strength was about 500 amp.

Analysis of new experimental material confirms the correctness of a hypothesis advanced by the authors previously regarding the mechanism of the passage of test material into the plasma of an impulse arc; according to this hypothesis, test material not only passes into the interelectrode gap of the source by fractional evaporation but also by periodic "injection" (sprinkling) of the molten mass of the test material.

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NEW COMPLEXONS

COMMUNICATION 4. SYNTHESIS AND STUDY OF COMPLEXONS OF THE TRIAZINE SERIES

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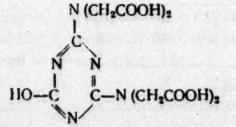
Continuing our studies [1-3] on the synthesis of new complexons, the work described in the present article was devoted to examining the effect of the nitrogen of the triazine ring on the capacity to form complex compounds. Schwarzenbach et al [4] have described complexons of the type

$$(HOOC{-}CH_2)_2N{-}(CH_2)_n{-}x{-}(CH_2)_n{-}N{-}(CH_2COOH)_2,$$

where x = O, S, and N; n = 2,3.

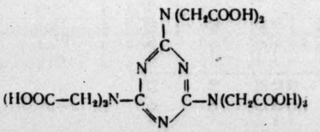
The introduction of atoms which are capable of coordinating with metals into the molecules of complexons, leads to an increase in their capacity to form complex compounds, and, in a number of cases, enhances the selectivity of the complexons for certain metal cations.

It was of interest to study the effect of heteroatoms in cyclic compounds. With this aim in view we synthesized the following complexons containing the 1,3,5-triazine ring



(I)

2-hydroxy-4,6-diamino-1,3,5-triazine-N,N,N',N'-tetracetic acid



(II)

2,4,6-triamino-1,3,5-triazine-N,N,N',N',N",N"-hexacetic acid

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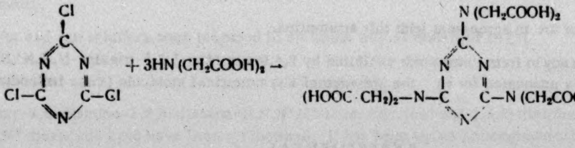
* Communication 3, see Zhur. Anal. Khim. 13, 31 (1958) [see C. B. translation].

TABLE 1

Half-wave Potentials for Cations in the Presence of 2-Hydroxy-4,6-diamino-1,3,5-triazine-N,N,N',N'-tetracetic acid (I), 2,4,6-Triamino-1,3,5-triazine-N,N,N',N',N",N"-hexacetic acid (II) and m-Phenylenediamine-N,N,N',N'-tetracetic acid (II), Relative to the Saturated Calomel Electrode

Ions	$E_{1/2}$ at pH 2,5				$E_{1/2}$ at pH 4,4				$E_{1/2}$ at pH 9,3				$E_{1/2}$ at pH 12.4			
	in the absence of complexon	In the presence of:			in the absence of complexon	In the presence of:			in the absence of complexon	In the presence of:			in the absence of complexon	In the presence of:		
		I	II	III		I	II	III		I	II	III		I	II	III
Pb^{2+}	—0,38	—0,52	—0,53	—0,44 —0,08	—0,43	—0,61	—0,47 —0,9 —0,2 —1,0	—0,62 —0,1	—0,18 —0,29	—0,49	disappears	—1,01 —0,38	—0, 7	—0,7	—0,71	—0,78 —1,40
Cu^{2+}	+0,02	—0,09 —0, 6	—0,10	—0,58	—0,02	—0,12 —0,60	—0,63	—0,58	—0,54	—0,39	—0,43	dis-appears	—0,05	dis-appears	—	—1,08
Cd^{2+}	—0,60	—0,68	—0,68	—0,78	—0,62	—0,72	—1,03	—0,68	—0,62	—0,63	—0,67	—0,68	—0,76	»	—1,42	—1,38
As^{III}	—1,02	—1,12	—1,09	—1,12	—	—	—1,24	—0,62 —1,2	—1,.7	—	—1,0	—1, 7	—	—	—1,40	—
Zn^{2+}	—1,08	—1,28	—0,40 —1,67	—1,18 —0,42	—1,09	—1,12	—	—1,09	—1,28	—1,28	—1,28	—1,28	—1,52	—1,52	—	—1,47
Ni^{2+}	—1,02	—1,28	—1,08	disapprs.	—1,12	—1,25	—1,24	—1,12	—1,01	—1,04	—1,0	—1,02	—1,37	—1,60	—	—1,38
Co^{2+}	—1,22	—0,64 —1,29	—1,25	—0,42 disapprs.	—1,15	—1,25	—1,20	—0,42 disapprs.	—1,21	—0,63 —1,25	—1,21	—1,21	—1,37	—1,40	—	—1,37
Mn^{2+}	—	—	—1,24	—0,56	—1,50	—1, 0	—1,03	—1,5	—1,58	—1,58	—1,0	—1,64	—	—	—	--
Ti^{IV}	—0,65 —0,97	—1, 2	—1,22	—0,65 —0,97	—	—0,87	—	—0,68	--	—	precpt.	turbidity	precpt.	—1,20	precpt.	turbidity
La^{III}	—0,62	—0,72	—0,73	—0,62	—0,72	—0,72	—1,04	—0,44	—0,68	—	—1,0	—	—	—	—	—
Tl^{+}	—0,46	—0,46	—0,44 —1,19	—0,48	—0,46	—0,48	—0,44 —1, 0	—0,48	—0,48	—0,48	—0,43 —0,66	—0,52	—0,46	—0,52	—0,43	—0,42 —1,08
Bi^{3+}	—0,12	—1,05	—	—	—0,21	—1,06	—	—	—	—	—	—	—0, 7	—1,20	—	—1,38 —

Complexons containing the 1,3,5-ring were synthesized by condensing cyanuric chloride with iminodiacetic acid:



The complex-forming properties of the new compounds were studied polarographically by determining the shift in the half-wave potentials, and calculating the instability constants of the complex compounds of a number of cations [5]. From the results given in Table 1 it follows that the complexons synthesized form a series of compounds with metal ions, among which the most interesting are the following:

1) 2-Hydroxy-4,6-diamino-1,3,5-triazine-N,N,N',N'-tetracetic acid forms compounds at pH 2.5 with the following ions Pb^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, Ni^{2+}, Mo^{VI} and Ti^{IV}; at pH 4.4 in addition to forming compounds with the ions already listed it also forms compounds with As^{III} and Mn^{2+}; at pH 9.35 it forms compounds with Pb^{2+}, Cu^{2+}, Cd^{2+}, As^{III}, Co^{2+}, Mo^{VI}; and at pH 12 with Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+} and Bi^{3+}.

2) 2,4,6-Triamino-1,3,5-triazine-N,N,N',N',N",N"-hexacetic acid forms compounds at pH 4.4 with the following ions: Pb^{2+}, Cu^{2+}, Mn^{2+}, Mo^{VI}, Ti^{IV}; at pH 2.5 in addition to the ions listed it also forms compounds with La^{III}, Tl^{+}, Zn^{2+}; at pH 9.3 it forms compounds with Pb^{2+}, Cu^{2+}, As^{III}, Mn^{2+}, Mo^{VI}, La^{III}; and at pH 12 with Cu^{2+}, Cd^{2+}, Ni^{2+}, Mo^{VI}.

In order to clarify the effect of the nitrogen atoms in the heterocycle on the stability of the complexes formed, we compared the properties of compounds I and II above, containing the 1,3,5-triazine ring, between each other and with m-phenylenediamine-N,N,N',N'-tetracetic acid which was synthesized for this purpose* and studied polarographically (see Table 1).

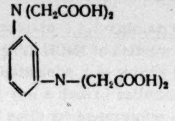


TABLE 2

Reciprocal Logarithms of the Apparent Instability Constants of the Compounds formed between Cations and I, II, and III at pH 2.5.

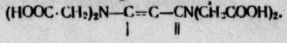
Cations	I	II	III
Pb^{2+}	4,75	5,08	3,63
Cu^{2+}	3,78	4,07	3,36
Zn^{2+}	6,7	7,1	3,4
La^{III}	5,08	5,56	3,05
Ti^{IV}	3,89	4,22	—

In order to get fuller characteristics for the complexons examined, the instability constants of their complexes with certain metals were determined polarographically (Table 2).

The shifts in the half-wave potentials of the complex compounds formed between the ions and I and II were greater in all cases than the shift obtained with complex compounds formed with III. Moreover, it should be noted that in the case of compound I there is an increased tendency to the formation of more stable complexes as compared with compound II.

A characteristic feature of I and II is the presence of the same group which is capable of forming complexes with metal cations

$$(HOOC\cdot CH_2)_2N-\underset{\|}{C}-N=\underset{|}{C}-N(CH_2COOH)_2.$$

It is natural to assume that the nitrogen of the triazine ring participates in complex formation. The shift in the half-wave potentials in this case should be similar for these two compounds and should be greater than the shift in the half-wave potential for m-phenylenediamine-N,N,N',N'-tetracetate,  $(HOOC\cdot CH_2)_2N{-}\underset{|}{C}{=}C{-}\underset{\|}{C}N(CH_2COOH)_2$.

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* m-Phenylenediaminetetracetic acid was synthesized by a method described in [6].

The results obtained are in agreement with this assumption.

The enhanced tendency to form compounds exhibited by 2,4,6-triamino-1,3,5-triazine-N,N,N',N',N",N"-hexacetic acid is probably accounted for by the presence of a symmetrical molecule (three iminodiacetic acid groups).

EXPERIMENTAL

Synthesis of 2-Hydroxy-4,6-diamino-1,3,5-triazine-N,N,N',N',-tetracetic Acid. To a suspension of 9.2 g of cyanuric chloride in 20 ml of water, cooled to 0°, is added with careful mixing half of the neutralized solution of iminodiacetic acid (7.5 g of iminodiacetic acid in 17 ml of 5 N NaOH). The temperature at the moment of addition of acid should not exceed +10°. After adding half of the volume of iminodiacetic acid, the reaction mass is kept for another three hours at a temperature of +5 to +10°, the pH of the solution being kept neutral all the time by means of universal indicator paper. To this solution is then added the other half of the neutralized iminodiacetic acid, and the temperature raised to 45-50°, and, while the alkalinity of the medium is continuously controlled with respect to phenolphthalein as an indicator, the reaction mass is kept for another five hours. The solution is filtered hot, it is then cooled and acidified with 10% hydrochloric acid to a pH of 2. After crystallizing, on cooling there is obtained 2-hydroxy-4,6-diamino-1,3,5-triazine-N,N,N',N'-tetracetic acid which is recrystallized from water.

The material is a white crystalline powder which is readily soluble in water and alkalis, sparingly soluble in in dilute alcohol, and insoluble in acetone, benzene, and chloroform.

$C_{11}H_{13}O_9N_5$ Found %: C 36.52; 36.42; H 3.89; 3.97; N 19.68; 19.52.
Calculated %: C 36.8 H 3.62 N 19.5.

Synthesis of 2,4,6-Triamino-1,3,5-triazine-N,N,N',N',N",N"-hexacetic Acid. 46 g of iminodiacetic acid is neutralized with a 20% solution of NaOH using universal indicator paper. A third of the neutralized acid solution is added with careful stirring to a suspension of 18.4 g of cyanuric chloride in 30 ml of water cooled to 0°. Addition of the acid is controlled in such a way that the temperature of the flask does not exceed +10°. The reaction mass is kept at this temperature for three hours while the pH of the solution is kept at about pH 7.

To this solution is then added the remainder of the neutralized iminodiacetic acid, the temperature of the flask is raised to 45-50° and kept at this temperature for one hour. The reaction mass is next heated to 95-100°, and, while the pH is kept at about 6-7, the reaction is allowed to continue for a further three hours. The solution is filtered hot, it is cooled and acidified with a 10% solution of hydrochloric acid to a pH of 2. On cooling, a crystalline precipitate of 2,4,6-triamino-1,3,5-triazine-N,N,N',N',N",N"-hexacetic acid separates out. This is filtered off and washed with iced distilled water until the wash liquors give no reaction for Cl⁻ ions. It is purified by repeated recrystallization from hot water. Yield 25 g.

2,4,6-Triamino-1,3,5-triazine-N,N,N',N',N",N"-hexacetic acid is a white crystalline powder which is readily soluble in hot water and alkali, it is sparingly soluble in cold water and dilute alcohol, and insoluble in acetone, benzene, chloroform, and ether.

$C_{15}H_{18}O_{12}N_6\cdot 2H_2O$ Found %: C 34.63; 34.88; H 3.44; 3.65; N 16.41; 16.54.
Calculated %: C 35.27 H 3.52; N 16.46.

A LP-55-A polarograph of the Heyrovsky type was used with a differentiating system during the determination of the purity of the reagents used, and also for interpreting poorly defined reduction waves.

The cathodes used were the usual dropping-mercury electrode with the following characteristics: m = 2.2 mg/sec, t = 1.8 sec, and an electrode in which the drop was compelled to drop off by means of a little spade attachment; the characteristics of this electrode were t = 4.2 sec, and m = 1.82 mg/sec without the spade attachment, and t = 0.52 sec with the spade attachment.

The anode was a saturated calomel electrode connected to the electrolyzer via a bridge filled with agar-agar and a saturated KCl solution. Hydrogen was passed through the solution for 10-15 minutes prior to taking polarograms in order to remove dissolved oxygen. The hydrogen ion concentration in the test solutions was controlled by means of a quinhydrone electrode, and, in a number of cases by means of a glass electrode, using a LP-5 potentiometer.

The buffer and test solutions were prepared in the same way as described in [1].

SUMMARY

2-Hydroxy-4,6-diamino-1,3,5-triazine-N,N,N',N'-tetracetic acid and 2,4,6-triamino-1,3,5-triazine-N,N,N',N',N",N"-hexacetic acid have been synthesized; it has been shown polarographically that these acids form compounds with a number of ions.

A comparison of the properties of the new complexones with those of m-phenylenediaminetetracetic acid has shown that the nitrogen of the hetero ring participates in the formation of compounds with metals.

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POLAROGRAPHIC DETERMINATION OF THE ALKALI METALS IN AQUEOUS AND AQUEOUS-ALCOHOLIC MEDIA IN THE ABSENCE OF A SUPPORTING ELECTROLYTE

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Studies of the polarograms of aqueous solutions of the alkali metals were initiated by Heyrowsky [1], who established many general conditions for the polarographic determination of the alkali metals; subsequently, these investigations were extended by Heyrowsky and by other research workers [2-8]. At present, determination of the alkali metals is carried out in a supporting electrolyte of tetraalkylmethyl-, ethyl-, and butylammonium bases or their halide salts. The compounds mentioned above are difficult to purify, and the purity of the supporting electrolyte (in order to get clearly defined polarograms) must be high.

TABLE 1

Comparison of the Concentrations of Lithium Chloride Solutions Determined by Various Methods

Determination polarographically, N.	Determination mercurimetrically, N	Difference, %
0,6309	0,6405	1,50
0,2693	0,2735	1,52
0,2281	0,2317	1,55
0,4351	0,4415	1,44
0,5453	0,5538	1,53
0,2385	0,2425	1,65

Since the first publications of Heyrowsky [1] there has been no information on the polarographic determination of the alkali metals in the absence of a supporting electrolyte. We thought it would be expedient to develop a technique for the determination of aqueous and aqueous-alcoholic solutions of the alkali metal chlorides in the absence of a supporting electrolyte. From a theoretical viewpoint, starting the problem in this way may appear rather strange at the first glance.

We were also interested in establishing the possibility of analyzing mixtures of alkali metals under the same conditions.

A Heyrowsky M-102 Czech micropolarograph was used for the work, the experiments were carried out at room temperature. The capillary had an internal diameter of 0.05 mm, the length being 20 cm.

The solutions of the alkali metal chlorides were prepared in twice-distilled water. The concentration of the original solutions was determined by weighing the calcined pure chlorides of the alkali metals and checking on them by argentometric titration. The limits of the concentration ranges used were 0.0005 N to 0.0070 N in aqueous media, and 0.0020 to 0.0140 N in aqueous-alcoholic media. The compensation setup of the apparatus was used for taking the polarograms. The potential applied to the rheocord was 4.8 volt for aqueous media and 6.4 volt for aqueous-alcoholic media.

As examples there are shown in Figs. 1 and 2 the polarograms for an aqueous solution of lithium chloride and potassium chloride. As is evident from these Figs., the polarograms are clearly defined, and their quality is completely satisfactory. Similar polarograms were obtained in aqueous-alcoholic media.

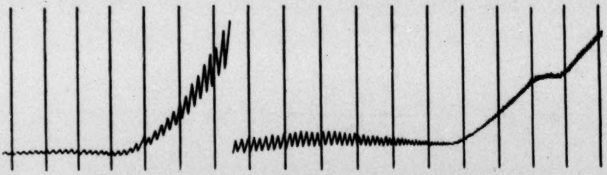

Fig. 1. Polarogram for a 0.0015 N aqueous solution of LiCl.

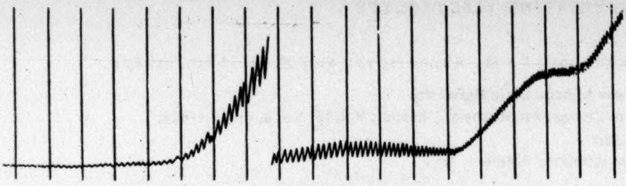

Fig. 2. Polarogram for a 0.0010 N aqueous solution of KCl.

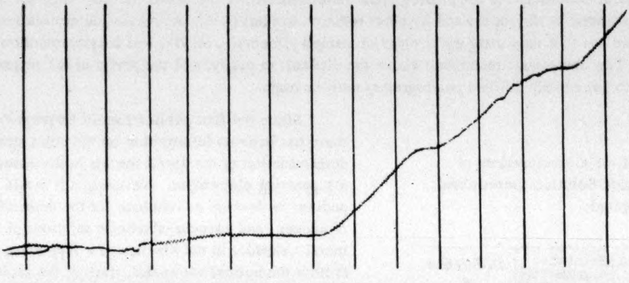

Fig. 3. Polarogram of a mixture of 0.0040 N KCl solution, 0.0060 N NaCl solution, and 0.0020 N LiCl solution in 95% methanol.

Since the resistance of the working solution is very high in the absence of a supporting electrolyte, part of the voltage applied to the rheocord was expended on the ohmic resistance of this solution. Accordingly, the half-wave potential of the alkali metals formally calculated on the basis of the rheocord voltage proved to be displaced towards the negative side with respect to the corresponding potentials observed in the presence of a supporting electrolyte. Thus, for an aqueous solution we obtained the following half-wave potentials: −3.82 volt for Li^+; −3.12 volt for K^+; and −3.08 volt for Na^+.

Within the concentration range which we studied there exists a linear relation between wave height and concentration.

Subsequently, a series of control polarographic measurements were carried out on the determination of large lithium concentrations (in aqueous solutions of lithium chloride) by appropriate dilution, while the chloride ion content was also determined in parallel by mercurimetric titration using diphenylcarbazide as the indicator.*

As is evident from Table 1 the error in the polarographic determination of the concentration of LiCl solutions

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* Data on the mercurimetric titration of lithium chloride was taken from the work of Yu. V. Kabankov and E. M. Timofeev.

TABLE 2

Relation between the Wave Heights of the Alkali Metals for Ternary Mixtures in a 75% Methanolic Medium

Mixture	Concentration ratio	Wave height ratio	Mixture	Concentration ratio	Wave height ratio
NaCl : KCl : LiCl	1 : 1 : 1	11 : 20,0	NaCl : KCl : LiCl	1 : 4 : 1	24 : 20,7
	2 : 1 : 1	16 : 18,5		1 : 5 : 1	27 : 21,5
	3 : 1 : 1	20 : 19,0	NaCl : KCl : LiCl	1 : 1 : 2	10 : 23,5
	4 : 1 : 1	23 : 19,5		1 : 1 : 3	11 : 34,0
	5 : 1 : 1	30 : 21,0		1 : 1 : 4	10 : 39,0
NaCl : KCl : LiCl	1 : 2 : 1	17 : 20,0		1 : 1 : 5	9 : 44,0
	1 : 3 ; 1	22 : 21,5			

lies within the limits ± 1.5% with respect to the determination by mercurimetric titration. It is obvious from a comparison of these two methods that it is possible to determine the alkali metals quantitatively in the absence of a supporting electrolyte polarographically.

An attempt was made to analyze a mixture of the alkali metals. For this purpose polarograms were taken of mixtures of alkali metal ions: sodium–potassium; sodium–lithium; ,sodium–potassium – lithium. It was found that only the sodium–lithium mixture gave two clearly defined waves. A break and a wave were obtained for the potassium–lithium mixture, while the sodium–potassium mixture just gave one common wave.

The height of the sodium and lithium wave on the polarogram of this mixture was not equal to the height of the wave for the individual metal ion of the same concentration. But, although these heights are not equal, there still exists a linear relation between these values and the concentration of the components of the mixture.

Replacement of water by an aqueous-alcoholic medium (95% and 75% methanol and 75% ethanol) improved the polarogram for the lithium–potassium mixture; instead of the break and a wave, two clearly defined waves were obtained. The potassium–sodium mixture gave one wave as before.

In the aqueous-alcoholic medium, as in water, the height of the wave for the individual metal in the mixture did not correspond to the wave height of the same metal, taken from a calibration curve for the individual alkali metal, although the linear relation betweeen the wave height and the corresponding concentration was maintained.

We also studied ternary mixtures with varying contents of each component in a 75% methanolic medium. In this case two waves were obtained on the polarogram: one for lithium and one for the mixture of sodium and potassium (Fig. 3). The height of the common wave varied with the changes in the ratio of the concentration of the sodium and potassium ions, but this change did not affect the wave height of lithium, in exactly the same way as the lithium concentration did not affect the combined wave of sodium and potassium (see Table 2).

Separate waves for sodium and potassium could not be obtained in ternary mixtures. However, on the basis that for Li–K mixtures in aqueous solutions in the absence of a supporting electrolyte, only a break and a wave are obtained, while in aqueous-alcoholic solutions in the absence of a supporting electrolyte two waves are obtained, it is possible to suggest that by choosing appropriate conditions for polarographic analysis, it should be possible to obtain individual waves for these metals in their mixtures.

We should like to thank A. N. Frumkin and E. N. Vinogradov for a number of valuable observations in preparing this article.

SUMMARY

Polarograms have been obtained for aqueous and aqueous-alcoholic solutions of the alkali metal chlorides in the absence of a supporting electrolyte.

It has been shown that it is possible to determine the ions of the individual alkali metals without using a supporting electrolyte. It has also been demonstrated that it is possible to obtain two clearly defined waves for

mixtures of Li and K in an alcoholic medium in the absence of a supporting electrolyte; this was not found possible when only an aqueous medium was used.

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FLAME PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF RUBIDIUM IN SILICATES

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The effect of the composition of the test material on the accuracy of the determination of elements by the flame photometric method can be eliminated by various techniques; for example, by comparing the composition of a standard solution with that of the test solution; by the method of additions, in which the standard is a known amount of the test element added to an aliquot of the test solution; by making use of the stabilizing (buffering) action of salts. The latter technique has the advantage over the two other methods that it does not require in each individual analysis the preparation of a new standard solution. Moreover, buffering can, in certain cases, permit the equilibrium of the processes which occur in the flame to be shifted so that there is an increase in the radiation intensity of the test element, thereby increasing the sensitivity of the determination.

In carrying out series of analyses on rocks and minerals, the advantages of the buffering method assume considerable importance.

The present article contains results of a quantitative study of the effect of the alkali metals on the radiation of rubidium in a flame, and the possibility is demonstrated of carrying out a flame photometric determination of small amounts of rubidium in silicates by buffering the test solution with potassium. A similar method has been developed for cesium [1].

The experiments were carried out on a spectrophotometric setup by means of the technique described in [1] at a wavelength of 794.8 mμ. The choice of the 794.8 mμ line was governed by the large distance by which it is separated from the potassium lines (768.5-769.9 mμ) as compared with the line 780.0 mμ. The effect of the Rb radiation of sodium, potassium, lithium, and cesium present in solution was studied. The Rb concentration of the solution was 2.76 μg/ml while the concentrations of the additives were varied from 25 to 6000 μg/ml (calculated in terms of the element) stepwise in amounts of 25, 50, 100, 1000 μg/ml and subsequently in intervals of 1000 μg/ml.

The presence of the alkali metals in the test solution led to a sharp increase (up to 7-38 times as much) in the rubidium radiation for high concentrations of the additives. Cs exhibited the greatest effect, and then K, Na, and Li. This is clearly evident from the curves relating the photocurrent to the concentration of the additives (Fig. 1).

The regularities observed agree with the assumption that the mutual effect of the alkali elements on the intensity of their radiation in the flame is connected with a change in the equilibrium in the ionization processes of these elements [2], the increase in intensity being determined by the suppression of the ionization process of one alkali metal by the other. For an equal ionic concentration of the additives, the effect shown is greater the greater the degree to which the influencing element is ionized. The sharp change in the radiation intensity of rubidium under the influence of additions of the alkali metals proceeds to a definite limit, beyond which further

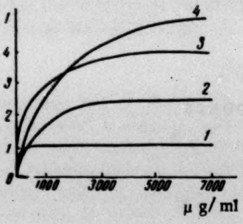

Fig. 1. Relation between radiation intensity (I) of rubidium (2.76 µ g/ ml) in an acetylene-air flame and the concentration (C) of impurities: lithium (1), sodium (2), potassium (3), and cesium (4).

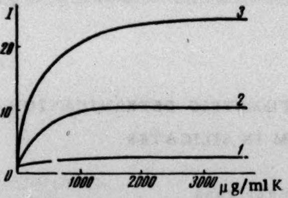

Fig. 2. Effect of potassium on the radiation intensity of rubidium (I) (λ = 794.8 mµ) in an acetylene-air flame. Rubidium concentration (µ g/ ml): 1) 2.5; 2) 17; 3) 175.

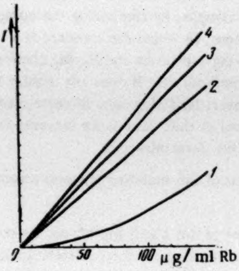

Fig. 3. Change in the concentration curves of rubidium under the influence of potassium. Concentration of potassium in the solution (µ g/ liter): 1) 0; 2) 500; 3) 1000; 4) 2500; I) the readings on the galvanometer scale.

increases in the concentration of the additives do not lead to any appreciable changes in the radiation intensity of rubidium. The value of the maximum radiation intensity depends on the element added. When a cesium salt was added, the maximum intensity was 30 times that in the absence of this salt, while on addition of a potassium salt it was 26 times greater, and 20 times and 7 times greater in the case of addition of sodium and lithium,respectively. The amount of the foreign element which had to be added to give this maximum intensity was 10,000 µ g /ml in the case of Cs, 3000 µ g/ ml for K, 2000 µ g /ml for Na, and 600 µ g/ ml for Li. Converted to ionic concentrations this is equal to (7-8) $\cdot 10^{-2}$g ion/ liter for all the elements.

The combined effect of the alkali metals on the radiation intensity of Rb was also studied. It was established that after adding more than 6,000 µ g /ml of cesium, addition of K, Na, and Li in any amount had no observable effect. In the presence of large amounts of potassium (2,500-3,000 µ g/ ml), Cs up to 1,000 µ g/ liter, and any amounts of Na and Li had no effect on the rubidium radiation. While when the solution contained 2,000 µ g/ liter of sodium, Cs up to 50 µ g /liter, K up to 250 µ g /liter, and Li in any amount had no effect on the rubidium radiation. In the presence of lithium (above 600 µ g/ liter), Cs in amounts up to 100 µ g/ liter, K in amounts up to 25 µ g/ liter, and Na in amounts up to 300 µ g /liter had no effect on the rubidium radiation.

The results given are in poor agreement with the assumption that the constancy of the radiation intensity of Rb in regions of high concentrations of the additives is the result of a switch over into the ionic state of all the rubidium ions reacting with the electrons of the prevalent alkali element (complete suppression of the ionization process [3]). Apparently, at a definite concentration of the prevalent component in the system $Me = M^{+} + e$, a stable equilibrium is set up, which can only be changed by equal concentrations of another alkali element with a lower ionization potential. Low concentrations of any alkali metal or equal concentrations of a component with a high ionization potential do not show any essential effect on this equilibrium. The constant number of free electrons in the flame stabilizes, in its turn, the number of non-ionized atoms of Rb which are capable of radiating. Thus, the radiation intensity of small amounts of rubidium can be buffered by any alkali element under conditions such that components with a higher degree of ionization than the buffer are contained in a considerably smaller amount.

TABLE 1

Determination of Rubidium in Rocks and Minerals

Sample	Found %	
	by the method of additions	by buffering with potassium
Quartz	0.005	0.006
The same	0.002	0.002
Feldspar	0.006	0.007
The same	0.050	0.045
Granodiorite	0.021	0.020
Muscovite	0.026	0.026
Muscovite granite	0.059	0.061
Double mica granite	0.020	0.023
Biotite	0.070	0.073

TABLE 2

Flame Photometric Determination of Rubidium in the Presence of Potassium

Taken, μg/ml	Found, μg/ml										Mean value, μg/ml	Error, %
0,2	0,16	0,17	0,2	0,21	0,2	0,18	0,21	0,2	0,17	0,23	0,19	5
2,0	2,0	2,0	1,9	1,8	2,0	2,1	1,9	1,8	2,0	2,2	1,97	1,5
20	19,5	19,2	19,5	19,3	20,2	20,3	20,0	20,4	18,6	19,5	19,6	2

For commensurate amounts of the interfering elements, the element chosen as the buffer should be the one with the highest degree of ionization. In this way, it is not only possible to achieve stable buffering, but it is also possible to get the maximum increase in sensitivity. Thus, for buffering rubidium one should take cesium, or, bearing in mind the cost of the latter and the insignificant amount of cesium in natural samples, potassium, whose concentration in silicates is usually high. Such replacement of Cs by K does not have any appreciable effect on the sensitivity and accuracy of the method, since the buffering action of cesium and potassium is similar.

In this connection therefore, the effect of potassium on Rb was studied in more detail. In Fig. 2 are shown curves relating changes in the radiation intensity of Rb and its concentration in solution (2.5, 17,175 μg/ml) under the influence of various amounts of potassium (25-4,000 μg/liter). This diagram, like the previous one, shows that the increase in the radiation intensity of Rb under the influence of potassium reaches a definite limit, beyond which further increases in potassium concentration do not lead to changes in the radiation intensity.

At a Rb concentration of 2.5 μg/liter, the radiation intensity increased 24-26 times, while for a Rb concentration of 17 μg/liter it increased about 10 times, and for a concentration of 175 μg/liter the intensity increased 2.5 times. This character of the change in the intensity of the Rb radiation under the influence of potassium has a favorable effect on the path of the standard curve (Fig. 3). Under the influence of potassium the standard curve for rubidium is straightened out; this considerably simplifies comparison of the test solution with the standard solution.

The effect of Ca, Mg, Sr, P, and Fe on the rubidium radiation was also studied. Of these elements, the one that showed the greatest effect was Ca, which increased the radiation of low concentrations (1-10 μg/liter) of rubidium by 80-70% and of higher concentrations (30-50 μg/liter) by 20-25%. In the presence of potassium, however, the effect of the elements listed is eliminated.

The effect of the bulk composition of the sample was checked by comparing the results of an analysis carried out by the method of buffering with potassium and the method of additions (Table 1). These experiments showed that the composition of the sample has no effect on the Rb radiation in the presence of large amounts of potassium.

As a result of these experiments it was established that by adding a definite amount of potassium to the test and standard solution before carrying out a flame photometric measurement, it is possible to determine hundredths and thousandths of a percent of Rb in silicate rocks and minerals without taking into account the composition of the sample. The experimental error amounts to 10-15%. The minimum amount of Rb that can be determined in solution is 0.1 μg/liter. Chemical preparation of the samples consists in decomposing them with hydrofluoric and sulfuric acids or by fusion with $CaCO_3$ and NH_4Cl.

Potassium is added to the test solutions without taking into account the potassium content of the sample, as long as its content in the sample is not greater than 1500 μg/liter. When the sample contains a large amount of potassium, the amount of the latter added should be decreased in order to avoid too high a background. During photometric measurements a correction is applied for the background resulting from the characteristic radiation from potassium and the other elements present in the sample. The results of the measurements are given in Table 2.

The method has been tested on a large number of samples of rubidium-containing materials: pegmatites, granites, micas, beryls, and has been introduced into practice at the analytical chemical section of the Institute of Mineralogy, Geochemistry, and Crystallochemistry of the Rare Elements of the Academy of Sciences, USSR.

Experimental Procedure. 0.5-1 g of sample is placed in a platinum basin and moistened with water, 0.4 ml of concentrated H_2SO_4, 15 ml of HF, and 2-3 drops of HNO_3 are added. The mass is heated to 70-80°. As the sample decomposes heating is increased, decomposition is completed on appearance of white sulfuric acid fumes. The residue in the basin is cooled, two ml of water and 0.1 ml of concentrated sulfuric acid are added and the mass heated until white fumes appear again. In order to make sure that all the fluorides have been removed, the mass is evaporated a third time with water. 25-30 ml of water is added and the whole heated until the salts have dissolved. The solution plus residue is transferred into a 50 ml standard flask and then diluted with water to the mark. The solution is filtered in portions through a dry filter into a beaker. The first portion is rejected, 20 ml is then taken from the main bulk of the filtrate and transferred to a 25 ml standard flask. To the latter is added 2.5 ml of potassium sulfate (25,000 μg K/ml) and the volume made up to the mark with water. After mixing, the solution is used for carrying out photometric measurements for determination of its Rb content (794.8 mμ). Photometric measurements are made at three positions of the drum: 1) 8-10° above the rubidium line; 2) on the rubidium line; 3) 8-10° below the rubidium line. Simultaneously with the measurements of the test solution, measurements are also carried out under the same conditions on a standard solution of rubidium sulfate to which K_2SO_4 has been added at the rate of 250 μg K/ml. The percentage content of rubidium in the test material is calculated by means of the formula:

$$\%\ \mathrm{Rb} = \frac{C_{\mathrm{standard}}\left(I_x - I_{\mathrm{background}_1}\right) \cdot 50 \cdot 25 \cdot 100}{\left(I_{\mathrm{standard}} - I_{\mathrm{background}_2}\right) \cdot 20Q \cdot 10^6}$$

where C_{standard} is the Rb concentration of the standard solution in μg/ml; Q is the weight of sample; I_{standard} is the deflection of the galvanometer needle in scale divisions during measurements of the standard rubidium solution (λ = 794.8 mμ); I_x ditto for the test solution; $I_{\mathrm{background}(12)}$ is the correction applied for the background, obtained as the mean arithmetic value of the two deflections of the galvanometer needle at the wavelengths which are longer and shorter than the rubidium wavelength (8-10° either side of the rubidium line).

For preparing a standard solution of rubidium sulfate, about 1 g of RbCl is dissolved in water in a 50 ml platinum basin. To the solution is added 2 ml of 4 N H_2SO_4. The contents of the basin are evaporated, first on a water bath, and then on a hotplate until a glassy mass is obtained which crystallizes on cooling; it is then heated over a burner with a weak red flame to constant weight. The salt is dissolved in distilled water and the solution transferred to a 500 ml standard flask in which it is made up to the mark with water. The exact amount of rubidium per ml of solution is calculated from the weight of rubidium sulfate. By dilution of the stock solution, working standard solutions of rubidium are prepared containing K_2SO_4: the initial K_2SO_4 concentration is 27.85 g K_2SO_4 in 500 ml H_2O (25,000 μgK/ml). The number of working solutions that need be prepared depends on the concentration range to be measured. In the range 0.2-100 μg/ml we used three standards: about 1 μg Rb/ml + 2,500 μg K/ml; about 20 μg Rb/ml + 2,500 μg K/ml; and about 80 μg Rb/ml + 2,500 μg K/ml.

SUMMARY

The effect of Cs, K, Na, Li, and some other elements on the radiation intensity of Rb (λ = 894.4 mμ) in an acetylene-air flame has been studied. It has been established that it is possible to enhance and stabilize the rubidium radiation by adding potassium.

An improved flame-photometric method which has been developed for the determination of rubidium in rocks and minerals permits determination of hundredths and thousandths of a percent of rubidium in samples, with an error of 10-15%, without preliminary separation of Cs, K, Na, Li, Ca, Sr, Mg, P, Fe.

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* Original Russian pagination. See C. B. translation.

DETERMINATION OF SMALL AMOUNTS OF SILVER IN THE DEVELOPED PHOTOGRAPHIC IMAGE

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During a study of some questions relating to the theory of the photographic process, there arose the necessity for an analytical chemical method which would enable silver to be determined fairly rapidly and simply in separate parts of the developed and fixed sensitogram obtained, e. g., on a FSR-4 sensitometer [1]. The method should permit the determination of $1 \cdot 10^{-5}$ g of metallic silver on an area of about 0.4 cm^2, with an error of not greater than 10%. The gelatin present in the film should not interfere with the determination. The time taken to carry out one determination should be such that a complete analysis of a sensitogram (21 areas) should not take more than a few hours. Existing methods [2-27] are either unsuitable or are not applicable to the problem under discussion. Apparently, the most suitable technique is the photometric method in which dimethylaminobenzylidenerhodanine, first synthesized by Andreasch and Zipser [28], is used as the reagent for the silver ion. The rhodanine method, because of its high sensitivity and simplicity of execution, has been used for the determination of small amounts of silver in order to solve various problems [29-36].

EXPERIMENTAL

Silver nitrate was recrystallized and calcined at 220-230° [37]. The stock silver nitrate solutions in 0.1 N HNO_3 had concentrations of 0.1% Ag and 0.01% Ag (1.575 g/liter and 0.1575 g/liter $AgNO_3$). The solutions used for constructing the calibration curves were prepared by diluting the stock solutions a short time prior to use.

In order to avoid adsorption of silver by glass [32], all the solutions were stored in vessels made from No. 23. 29 glass or from pyrex as long as no heating was required; when heating had to be resorted to quartz vessels were used. A stock 0.01% solution of the rhodanine was prepared by dissolving the reagent in pure ethanol.

A differential photoelectriccolorimeter with a selenium photoelement (FÉK-M) [38] was used for measuring the light absorption of the silver-rhodanine suspensions. Absorption measurements were carried out in cuvettes with a layer thickness of the solution of 8 mm and with a capacity of 2.5 ml. The absorption of the suspensions was measured relative to air, i.e., no cuvette was placed in the reference beam of the photocolorimeter. The operating value of the optical density taken for determining the silver concentration was the value obtained after substracting the optical density of the corresponding cuvette containing water or control solution, which had been measured in turn with respect to air.

The maximum absorption of the suspensions was found to lie at 470-480 mμ. The most suitable light filter in this case is a blue filter made from SS-8 glass. The calibration curves used for determining silver in the test solutions were constructed on the basis of the optical density of standard solutions obtained under the same conconditions as those used for the test solutions.

Establishment of the Conditions Necessary to Carry out an Analysis

The optimum concentrations of nitric acid and rhodanine in the test solution were found to be 0.095 N HNO_3

TABLE 1

Silver Concentration of the Test Solution C_{Ag}, μg/ml																
Date of Measurement						mean C_{Ag}	absolute error μg/ml	error (relative)%	date of measurement				mean C_{Ag}	absolute error, μg/ml	error (relative),%
27/X	29/X	20/X	30/X	30/X	30/X				20/XI	20/XI	21/XI	21/XI			
—	—	0,14	0,16	0,15	0,15	0,15	±0,005	±3,3	0,43	0,42	0,47	0,48	0,45	±0,025	±5,6
—	0,40	0,42	0,41	0,45	0,44	0,43	±0,018	±4,2	0,53	—	0,53	0,55	0,54	±0,010	±1,9
0,91	—	1,02	0,97	0,95	—	0,96	±0,032	±3,4	0,88	0,84	0,81	0,82	0,84	±0,022	±2,7
—	1,29	1,23	1,33	1,27	1,32	1,29	±0,030	±2,3	0,96	0,87	0,90	0,95	0,92	±0,035	±3,8
1,73	—	1,77	1,70	1,73	1,79	1,74	±0,028	±1,6							
—	1,88	1,87	1,73	1,84	—	1,83	±0,050	±2,7							

and 0.00075% rhodanine.

Experiments showed that the values of the optical density of solutions containing gelatin ($2 \cdot 10^{-3}$ g/liter) are high because of increased scattering. However, the values of the absorption, expressed relative to the absorption of the corresponding control solutions, agreed among themselves, irrespective of the presence of gelatin. Accordingly, the fact that gelatin is present does not interfere with the use of the rhodanine method.

In order to be able to carry out an analysis of a sensitogram rapidly and without excessive loss, it was desirable to dissolve the silver contained in the field of the sensitogram directly in nitric acid, by heating, and, at the same time without detaching the film. Appropriate experiments showed that careful heating of the solutions until they were boiling gently did not affect the absorption of the silver-rhodanine suspensions.

At the same time it was found that the presence in the standard solutions of lumps of photographic film completely free from silver salt could favor some increase in the absorption of the suspension. Accordingly, turnings of unexposed, carefully fixed, and well-washed and dried pieces of film with a diameter of 5 mm (0.2 cm^2) were introduced into the solutions to be used for the calibration. By doing this experiment it was found that lumps of film have no significance whatever the volume of solution. Only at concentrations of silver higher than 1 μg/ml was there observed a tendency to a decrease in absorption in the case where one circle of film was placed in 50 and 100 ml of solution. We used a calibration curve obtained on measuring solutions containing one piece of film per 50 ml, since at concentrations of silver greater than 0.6 μg/ml, the volume to which it was diluted was not less than 50 ml. At a silver concentration of 0.03 μg/ml the value of the optical density with respect to the control solution was equal to 0.005, while for a silver concentration of 0.05 μg/ml it was 0.010. Thus, a change of 0.02 μg/ml insilver concentration led to a change of 0.005 in the optical density. The sensitivity of the apparatus in this part is 0.5 galvanometer scale division for $\Delta D = 0.001$. Accordingly, the limiting concentration can be regarded as 0.004 μg/ml. In order to increase the reliability of the experimental results, we considered that the sensitivity of the reaction is not equal to this limiting concentration, but to 0.04 μg/ml. Since the cuvettes we used could hold 2.5 ml of solution, then it should be possible to determine 0.10 μg of silver in the area of film taken.

The experimental error in determining silver was established by carrying out parallel measurements of the absorption of suspensions after adding rhodanine to separate aliquots of silver-salt solutions; it was found to be 1-6%. Measurements were carried out on solutions with silver concentrations ranging from 0.15 to 1.8 μg/ml (Table 1).

The reproducibility of the experiments is illustrated by the coincidence between the calibration curves obtained on different days (Fig. 1), and also by the values of the relative errors obtained in parallel experiments (Table 2). Here are included errors connected with the heterogeneity of the layer in the field of the sensitogram, which, in turn, may be the result of both uneven flow of the photographic emulsion and of uneven treatment of the layer after exposure.

TABLE 2

Reproducibility of the analysis								Panchrome type 10							
Experiment No. 47				Experiment No. 55				Experiment No. 57				Experiment No. 54			
D of the layer	D of the solution	C_{Ag} μg/ml	%	D of the layer	D of the solution	C_{Ag} μg/ml	%	D of the layer	D of the solution	C_{Ag} μg/ml	%	D of the layer	D of the solution	C_{Ag} μg/ml	%
0,43	0,135 0,126	0,60 0,55	±4,3	0,22	0,058 0,057	0,10 0,099	±0,5	1,79	0,177 0,181	0,87 0,89	±1,1	1,3	0,149 0,135 0,139	0,73 0,65 0,67	±4,4
0,63	0,115 0,127	0,47 0,54	±7,0	0,32	0,069 0,075	0,17 0,20	±8,1	2,19	0,190 0,183	0,95 0,91	±2,1				
1,02	0,194 0,190	0,98 0,95	±1,6	0,55	0,073 0,073	0,19 0,19	±0	2,46	0,181 0,195	0,91 0,99	±4,2	1,8	0,159 0,172 0,169	0,81 0,89 0,87	±3,5
1,49	0,210 0,206	1,13 1,07	±2,7	0,92	0,136 0,173	0,60 0,84	±16,6	2,68	0,172 0,167	0,83 0,80	±1,8				
1,98	0,171 0,171	0,82 0,82	±0	1,26	0,142 0,124	0,64 0,53	± 9,4								
2,38	0,186 0,186	0,93 0,93	±0	1,47	0,144 0,137	0,65 0,61	± 3,2								
2,60	0,191 0,189	0,96 0,96	±0,5	1,69	0,155 0,150	0,73 0,69	± 2,8								
				2,04	0,174 0,171	0,82 0,80	± 1,2								

TABLE 3

Optical density of the sensitogram field, D	Amount of 3 N HNO_3 used for dissolving the silver, ml		Final volume of the test solutions (before addition of the rhodanine), ml	
	Panchrome type 10 (with high silver content)	MZ positive (with low silver content)	Panchrome type 10	MZ positive
0,01—0,1	0,17	0,17	5	5
0,1 —0,5	0,67	0,67	20	20
0,5 —1,0	1,67	0,67	50	20
1,0 —1,5	3,33	1,67	100	50
1,5 —2,0	3,33—6,67	1,67	100—200	50

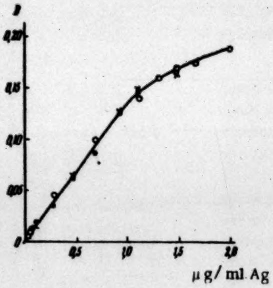

Fig. 1. Calibration curves. O) An experiment from 12/XI; •) an experiment from 22/XI; x) an experiment from 1/XII.

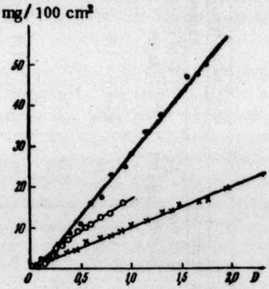

Fig. 2. •) Panchrome type 10; O) AM-35 negative; x) MZ positive.

In addition, Table 2 contains the results of parallel determinations of silver contained in different places of a uniformly exposed layer (experiment No. 54). As is evident from the Table, the mean experimental error lies within the limits 3-4%.

It is clear from Fig. 1 that the solutions conform to Beer's law within the range 0.004 to 1 μg/ml.

Experimental Procedure. From each area of the sensitogram was cut out a circular piece of film 5 mm in diameter by means of a special punch. These pieces of film were placed in quartz test tubes. Into each of these test tubes was introduced 3 N HNO_3 in various amounts depending on the expected silver content. We tried to ensure that the value of the optical density of the solutions measured lay within the limits D = 0.08-0.2. This corresponds to a silver concentration of 0.1 to 1.0 μg/ml.

On the basis of these considerations, Table 3 contains the recommended approximate amounts of nitric acid that should be added for dissolving the silver in films with different silver content of the emulsion. In addition, the Table also contains the corresponding final volumes of the test solutions, in separate portions of which the absorption is measured after addition of the rhodanine. The nitric acid concentration after dilution should be 0.1 N in all the test tubes.

The silver was dissolved by heating until a clear solution was obtained. The solutions were diluted after cooling. To separate aliquots of these solutions was added a 0.01% alcoholic solution of rhodanine at the rate of 0.4 ml of rhodanine per 5 ml of silver solution, prior to measurements. The solutions were carefully, and at the same time thoroughly mixed (without any shaking), they were then poured into the cuvette and their optical density measured every 1.5 to 5 minutes (since the optical density does not immediately reach its maximum values) for 10-20 minutes, depending on the silver concentration. The maximum values, which also proved to be the most stable, were used for subsequent calculations. In the periods between the measurements of optical density the cuvette plus suspension was shielded from light.

The silver concentration was found from the values of the optical density by using the calibration curves. Knowing the volume of solution in which the silver from a known area (0.2 cm^2) film had been dissolved, the amount of silver found on the sensitogram field (0.4 cm^2) was calculated in terms of g per 100 cm^2.

Results. We have carried out analyses of a large number of sensitograms obtained on films of emulsions with various silver contents, and with different sizes of microcrystals.

In Fig. 2 are shown the mean results for these sensitograms expressed in mg of silver per 100 cm^2 for various values of the optical density of the layer.

It is clear from the diagram that for different types of film the amount of silver contained in the field of a sensitogram with equal optical density is also different.

I should like to thank G. P. Faerman for valuable advice given in carrying out the work described here.

SUMMARY

Conditions have been worked out for determining silver by means of dimethylaminobenzylidenerhodanine in the developed photographic image.

The method permits determination of 0.04 μg of silver in one ml of solution, or $5 \cdot 10^{-5}$ g of silver contained in 100 cm^2 of a test layer. The experimental accuracy varies within 1-6% for silver contents of 0.15-2.0 μg or $2 \cdot 10^{-4}$ - $25 \cdot 10^{-4}$ g per 100 cm^2.

The reproducibility is 3-4%.

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THE MUTUAL EFFECT OF ELEMENTS ON RADIATION INTENSITY IN THE FLAME

COMMUNICATION 2. COMPOUNDS WHICH ARE FORMED DURING THE EXTINCTION OF CALCIUM AND STRONTIUM RADIATION BY ALUMINUM, ZIRCONIUM, AND URANIUM*

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It is known that during the flame-photometric determination of the alkaline earth metals, extinction of their radiation is observed when aluminum salts are present [1-3]. When sufficiently high concentrations of aluminum salts are used the calcium and strontium radiation drops almost to zero, and this can be used for determining alkaline metals present as impurities in Ca and Sr salts, since, under such conditions, interference from the background arising from the Ca and Sr salts in the region of the analytical lines of the alkaline metals can be eliminated [4-5]. On the other hand, when Ca and Sr are to be determined in various materials, it is essential that aluminum be removed from the test solution [6-7], or its effect is compensated by adding large amounts of a salt of another alkaline earth element [8, 9]. In addition to aluminum salts, an extinguishing effect on calcium and strontium radiation is also shown by the salts of a number of other elements – the strongest are Zr [10], Be, V, Th, Ti, U, and Cr [11-13]. It has been suggested that the extinguishing effect of the salts of these elements depends on the formation of compounds of the mixed oxides of these and the alkaline earth metals in the flame, and that this leads to a decrease in the concentration of Ca and Sr atoms in the flame gases, and to a decrease in their radiation intensity [3]. Using a method in which two sprayers were used for feeding one burner, we have showed that the probable reason for the depressing action of Al salts on the radiation intensity of Ca and Sr is the formation in the flame of low-volatile compounds between Al_2O_3, CaO, and SrO at the moment of evaporation of a drop of the aerosol of the test solution passing into the flame; a drop in the radiation intensity of Ca and Sr is not observed when the Al salt is introduced into the flame through another sprayer; this testifies to a breakdown in the passage of Ca and Sr atoms into the flame [14]. A similar conclusion has been made independently of us [8].

It was of interest therefore to obtain results on the composition of the compounds formed in flame gases between Ca(Sr) and Al or other extinguishing elements. Hitherto, in this connection, only hypotheses have been advanced; thus, it has been assumed [15] that Ca and Al form an aluminate with the composition $CaAl_2O_4$. However, in the case of the extinction of the radiation of the alkaline earth metals by chromium, it could be concluded that in the compound formed one atom of chromium corresponds to one atom of the alkaline earth metal [13], since, at such a ratio, extinction of the radiation is a maximum, and does not change on increasing the chromium concentration further. The method used for this purpose – studying the drop in the intensity of the

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* For communication 1 see [14].

TABLE 1

Effect of Zirconium and Uranium on the Intensity of Calcium and Strontium Radiation when Zr and U are Introduced in the Same Solution as Ca and Sr, and when Zr and U are Introduced through Another Sprayer

Concentration of element, M		Radiation intensity of Ca(Sr) as a % of the intensity in the absence of Zr (U)			
Test element	Foreign element	introduced in the same solution	introduced through the other sprayer	introduced in the same solution	introduced through the other sprayer
		acetylene frame		propane - butane flame	
Ca, 10^{-2}	Zr, 10^{-2}	65	98,5	50	95,5
Ca, 10^{-3}	Zr, 10^{-3}	45	98	43	99
Ga, $2{,}5\cdot10^{-3}$	U, $2\cdot5\cdot10^{-3}$	73,7	96	88,5	109
Sr, 10^{-3}	Zr, 10^{-3}	21	100	0	100
Sr, $2{,}5\cdot10^{-3}$	U, $2{,}5\cdot10^{-3}$	53	93	51,5	98,5

TABLE 2

The Solutions Used for Determining the Composition of the Compound Formed between Sr and Zr

Solution No.	Taken, ml		Concentration		Solution No.	Taken, ml		Concentration
	$2\cdot10^{-3}$ *M* Sr	$2\cdot10^{-3}$ *M* Zr	$X\cdot10^{-3}$ *M* Sr	$X\cdot10^{-3}$ *M* Zr		$2\cdot10^{-3}$ *M* Sr	water	$X\cdot10^{-3}$ *M* Sr
1	20	—	2	—	1′	20	—	2,0
2	18	2	1,8	0,2	2′	18	2	1,8
3	16	4	1,6	0,4	3′	16	4	1,6
4	14	6	1,4	0,6	4′	14	6	1,4
5	12	8	1,2	0,8	5′	12	8	1,2
6	10	10	1,0	1,0	6′	10	10	1,0
7	8	12	0,8	1,2	7′	8	12	0,8
8	6	14	0,6	1,4	8′	6	14	0,6
9	4	16	0,4	1,6	9′	4	16	0,4
10	2	18	0,2	1,8	10′	2	18	0,2
11	0	20	0	2,0	11′	0	20	0

TABLE 3

Corrections Applied during Construction of the Curve by the Isomolar-Series Method. Total Concentration Ca+ Zr = 10^{-2}M. Acetylene Flame. Photometric Measurements Made on the Basis of the Line Ca 422.7 mμ

Solution No.	Concentration of the Ca solution		Photocurrent I′, %	Ca solutions (mixed with Zr)			Value characterizing formation of a compound, ΔI′ (A − B)
	$X\cdot10^{-3}$ *M*	% of the max. (A)		Ca conc. × 10^{-3}	photocurrent I′, %	Ca conc. found, % (B)	
1	10	100	100	10	100	100	0
2	9	90	93	9	87	80	10
3	8	80	87	8	71,5	60	20
4	7	70	77	7	57,5	47	23
5	6	60	71,5	6	38,5	30	30
6	5	50	61	5	21,4	16,5	33,5
7	4	40	48,5	4	21,0	16,0	24
8	3	30	37,5	3	15,2	11,0	19
9	2	20	26,5	2	7,7	5,0	15
10	1	10	13,5	1	2,5	1,5	8,5
11	0	0	0	0	0	0	0

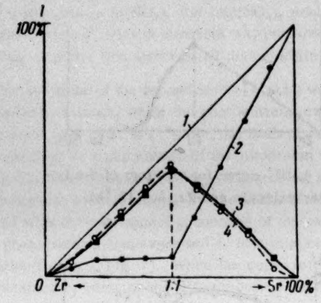

Fig. 1. Determination of the ratio between the number of atoms in the compound Sr–Zr by the isomolar series method. Total concentration, $2 \cdot 10^{-3}$ M; acetylene flame (Curves 1-3) and propane-butane flame (Curve 4). 1) Calibration curve for Sr; 2) curve for the solutions of the isomolar series; 3 and 4) difference curves.

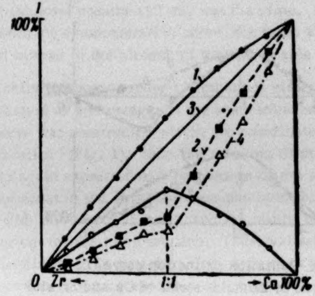

Fig. 2. Determination of the ratio between the number of atoms in the compound Ca–Zr by the isomolar series method. Total concentration, Ca + Zr = 10^{-2} M, acetylene flame. 1) Calibration curve for Ca; 2) curve for the solutions of the isomolar series; 3) corrected calibration curve; 4) corrected curve for the solutions of the isomolar series; 5) difference curve.

alkaline earth metal with increasing concentration of the foreign element – could not be used for our purpose, since the drop in the radiation intensity with increasing concentration of the foreign element proceeded gradually. Accordingly, we used the isomolar series method for determining the composition of the compounds of Ca and Sr with Al, Zr, and U.

Apparatus and Original Solutions. A flame spectrophotometer described earlier [11] was used, this consisted of a type UM-2 universal monochromator, type FÉU-19 and FÉU-22 photomultipliers, and a mirror galvanometer; the flames used were mixtures of acetylene and propane-butane with air. In order to clarify the nature of the interaction between zirconium and uranium salts and Ca and Sr a burner was used into the flame of which the aerosol was introduced through two separate sprayers, each provided with its own spraying chamber [14].

The original solutions of calcium nitrate were prepared by dissolving an aliquot of dried calcium carbonate (chemically pure) in nitric acid, while the strontium nitrate solution was prepared from crystalline, analyzed $Sr(NO_3)_2 \cdot 4H_2O$. Aluminum nitrate solution was prepared from $Al(NO_3)_3 \cdot 9H_2O$, while zirconium and uranyl nitrate solutions were prepared from zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$ and U_3O_8, respectively, by treatment with nitric acid. The zirconium and aluminum content of the salts was checked gravimetrically, and was found to coincide, within the limits of experimental error, with the theoretical value.

Establishment of the Nature of the Interaction Between Ca or Sr Salts and Zr and U. By means of a photometer provided with a burner with two sprayers, comparisons were made of the readings obtained for solutions of Ca (Sr) and the readings for the same solutions, containing, in addition, zirconium (uranium), and those for solutions not containing Zr (U), but in which a solution of a zirconium (uranium) salt was introduced simultaneously through the other sprayer into the flame. The results obtained are given in Table 1. Photometric measurements were made on the basis of the resonance lines (Ca 422.7 mμ and Sr 460.7 mμ) when an acetylene flame was used, and on the basis of the peaks of the molecular bands when a propane-butane flame was used (Ca 622 mμ and Sr 680 mμ).

As is evident from Table 1, the picture is the same as that observed in the case of aluminum [14], zirconium (uranium) salts depress the radiation intensity of calcium and strontium only when they are introduced into the flame in the same solution, and have hardly any effect when they are introduced into the flame through another sprayer. As indicated already [14], the probable reason for this effect is the retardation of the passage of calcium or strontium into the flame as the result of the formation of low-volatile compounds with zirconium (uranium) at

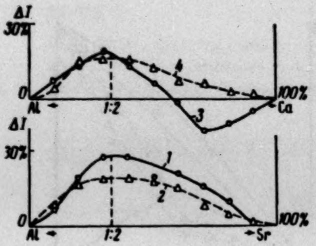

Fig. 3. Radiation extinction curve (ΔI) for solutions of isomolar series of Ca and Sr with Al. 1) Sr–Al, total concentration $\Sigma = 10^{-3}$M, propane-butane flame; 2) Sr–Al total concentration $\Sigma = 10^{-3}$M, acetylene flame; 3) Ca–Al, $\Sigma = 2 \cdot 10^{-3}$M, propane-butane flame; 4) Ca–Al, $\Sigma = 2 \cdot 10^{-3}$M, acetylene flame.

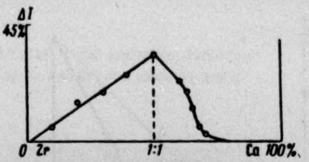

Fig. 4. ΔI' curve for solutions of the isomolar series Ca and Zr, $\Sigma = 10^{-2}$M.

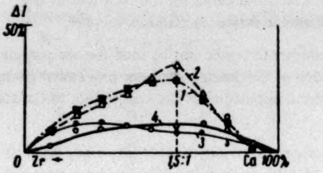

Fig. 5. ΔI' curve for solutions of the isomolar series Ca and Zr (chlorides). 1) Propane-butane flame, $\Sigma = 2 \cdot 10^{-3}$M; 2) propane-butane flame, $\Sigma = 5 \cdot 10^{-4}$M; 3) acetylene flame, $\Sigma = 2 \cdot 10^{-3}$M; 4) acetylene flame, $\Sigma = 5 \cdot 10^{-4}$M.

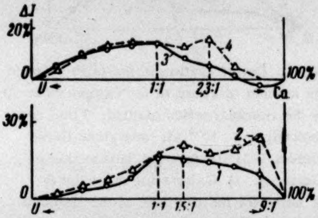

Fig. 6. ΔI' curve for solutions of the isomolar series Ca and U. 1) Acetylene flame, $\Sigma = 5 \cdot 10^{-3}$M; 2) acetylene flame $\Sigma = 10^{-2}$M; 3) propane-butane flame, $\Sigma = 5 \cdot 10^{-3}$M; 4) propane-butane flame, $\Sigma = 10^{-2}$M.

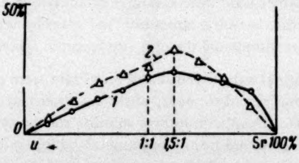

Fig. 7. ΔI' curve for solutions of the isomolar series Sr and U, $\Sigma = 10^{-2}$M. 1) Acetylene flame; 2) propane-butane flame.

the moment of evaporation of drops of solution on passing into the flame. When the solution of a zirconium (uranium) salt is introduced into the flame through another sprayer, the zirconium (uranium) proceeds independently of the salts of the alkaline earth metals and cannot form compounds with the latter.

Determination of the Ratios between the Number of Metal Atoms in the Compounds Formed. The isomolar series method of Ostromyslenskii-Job was used for determining the composition of the low-volatile compounds formed. Depression of the radiation intensity of the element in the flame was used as the value characterizing the formation of the compounds.

During these measurements corrections were applied for the absorption of radiation in the flame, or for changes in the efficiency of the operation of the sprayer for various concentrations of the element, by simultaneous construction of the corresponding concentration curve. The experimental technique [16] can be illustrated by the following example of the determination of the compound of Sr and Zr.

A series of solutions containing $Sr(NO_3)_2$ and $ZrO(NO_3)_2$ in various concentrations were prepared so that the total concentration of both components amounted to, for example, $2 \cdot 10^{-3}$M. For this purpose varying volumes of $2 \cdot 10^{-3}$M solutions of $Sr(NO_3)_2$ and $ZrO(NO_3)_2$ were mixed so that the total volume (20 ml) was the same. At the same time a second series of solutions was prepared in order to construct a concentration curve, the same amounts of $Sr(NO_3)_2$ as in the first series being taken, while water was used instead of the zirconium solution (Table 2).

The solutions of the second series (1'-11') were photometrically measured amongst themselves either according to Sr lines or bands, while the photocurrent readings were expressed as percentages of the stock solution with a concentration of $2 \cdot 10^{-3}$M (1'). On the basis of these results a curve was constructed within the coordinates "photocurrent readings as a percentage of the maximum value – concentration" (Fig. 1). Next the solutions of the first series (1-11) were measured amongst themselves, and the readings again expressed as a percentage of the solution with the highest concentration. By another method each of the solutions of the first series was photometrically measured with the corresponding solution of the second series (2 with 2', 3 with 3', etc.), and the results obtained for the photocurrents also expressed as percentages of the photocurrent for the main solution. These values lie on a curve (Curve 2, Fig. 1). When the curve for solutions not containing Zr is a straight line, as in our case, the curve obtained by plotting the differences on the ordinate as a function of the composition of the solution (Curve 3, Fig. 1), gives a direct indication of the composition of the compound.

When the curve for the solution is not a straight line then a correction has to be applied for the value of the photocurrent obtained with solutions containing Zr. The values found for the concentration are conveniently expressed as percentages of the maximum; for this purpose the scale is given in percentages along the abscissa (Fig. 2). The method used for calculating is given in Table 3 for the case of the determination of the compound formed between Ca and Zr.

In Fig. 3 are shown curves obtained during the determination of the composition of the compound formed between Ca and Sr with Al; the salts taken were the nitrates. In both flames the maxima of the curves correspond fairly accurately to a molar ratio of Ca(Sr) : Al = 1 : 2.

Probably, the extinction of Ca and Sr radiation in a flame in the presence of aluminum salts is connected with the formation of the compounds $CaAl_2O_4$ and $SrAl_2O_4$.

In the case of calcium and aluminum when a propane-butane flame (Curve 3, Fig. 3) flame is used, one has to assume the existence of yet another compound with a molar ratio of Ca : Al = 3 : 1, which is more volatile than calcium oxide.

The maximum in Fig. 4 (and also in Figs. 1 and 2) corresponds to a molar ratio of Ca(Sr) : Zr = 1 : 1 (taken as their nitrates). Thus, the probable composition of the compounds formed in the flame corresponds to the formulas $CaZrO_3$ and $SrZrO_3$.

In the case of solutions of calcium chloride and zirconium oxychloride (Fig. 5), a compound which is poorer in zirconium is formed; the maximum of the curves in the case of a propane-butane flame is found at a ratio of Ca : Zr = 3 : 2 (the compound $Ca_3Zr_2O_7$ is probably formed). In the hotter acetylene flame, depression of the radiation intensity of Ca is not great and there is no sharp maximum on the curve. Apparently, in the presence of chlorides, zirconium partially evaporates in the form of its chloride, it evaporates in this form to a greater extent than calcium.

In Figs. 6 and 7 are shown the curves obtained during the determination of the composition of the compound formed with uranium. In the case of calcium, extinction of its radiation is not great, and no conclusion can be made as to the formation of one definite compound. In addition to the maxima observed on certain curves for a ratio of Ca : U = 1 : 1, there are also maxima at another ratio of the number of atoms of Ca and U. In the case of Sr and U there is preferential formation of a compound in which the ratio Sr : U = 3 : 2, which could also indicate the formation of a mixture of compounds with a ratio of Sr : U = 1 : 1 and 2 : 1.

SUMMARY

Extinction of the radiation of calcium and strontium is only observed when Zr and U are present at the same time in the Ca and Sr solutions, and is not observed when Zr and U are introduced into the flame separately from the solutions of the Ca and Sr salts. This gives a basis for assuming that the extinction is connected with formation of poorly volatile compounds of Ca(Sr) with Zr and U at the moment when the drops of the aerosol of the solution evaporate in the flame.

The isomolar series method enables one to establish the composition of the compounds formed in the flame, by using the decrease in the radiation intensity of the elements in the flame as a factor characterizing the formation of compounds.

The reason for the extinction of radiation on using solutions of Al and Zr nitrates is the probable formation of of the compounds Ca(Sr)Al_2O_4 and Ca(Sr)ZrO_3. In the case of Ca and U, presumably, there is formed a mixture of compounds of different composition, while in the case of Sr and U there is formed a compound in which the molar ratio of Sr : U = 3 : 2.

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[*] Original Russian pagination. See C. B. translation.

PHOTOMETRIC DETERMINATION OF CERIUM BY MEANS OF O-TOLIDINE

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Several analytical methods are known for cerium [1-9]. The present article is devoted to still one more possibility – a comparatively more selective and sensitive determination of cerium in its quadrivalent state by means of o-tolidine (3,3'-dimethylbenzidine). The reaction for the qualitative detection of cerium by means of o-tolidine has been known for a long time. Until recently, however, it has not been used for the quantitative determination of cerium.

Cerium is removed from interfering components together with the rare earths in the form of oxalates. When the test material does not contain rare earth elements, lanthanum nitrate is added and the oxalates precipitated.

For our work we used a solution of $La(NO_3)_3$ containing 12 mg per ml.*

Cerium was coprecipitated with lanthanum under the following conditions: to the solution containing cerium, 1 ml of lanthanum nitrate solution was added. After diluting with water to 7-8 ml, cerium and lanthanum were precipitated with an equal volume of a cold, saturated solution of oxalic acid. The precipitate obtained was filtered on the next day through a filter tube [10]; it was dried and then calcined at 800-900°. The precipitate calcined in this way contains cerium and lanthanum oxides.

According to the results of Meyer and Aufrecht [11], concentrated sulfuric acid converts CeO_2 into anhydrous cerium sulfate $Ce(SO_4)_2$. When the CeO_2 is moist or contains $Ce(OH)_4$, then cerous ceric sulfate $Ce^{III}Ce^{IV}(SO_4)_4$ is formed. In more dilute solutions various compounds are formed, the composition of which varies with the pH of the medium; at sufficiently high dilution $Ce_2(SO_4)_3$ is obtained. Bearing in mind this last fact, we dissolved the calcined precipitate in 10-12 drops of hot concentrated sulfuric acid free from reducing agents. Under these conditions anhydrous, yellow $Ce(SO_4)_2$ was obtained, which was almost insoluble in concentrated H_2SO_4. To this was added 1 ml of a 0.05% solution of o-tolidine in 10% sulfuric acid. After diluting to 100 ml, the solution was measured photometrically. It was found thereby that the amount of o-tolidine does not affect the color intensity.

The optical density was measured in a FÉK-M colorimeter with a blue filter (transmission maximum at 410 mμ).

From Fig. 1 it follows that the solution conforms to Beer's law at concentrations up to 3 μg Ce/ml. The molar extinction coefficient is about 9,500. The reaction with o-tolidine is 20 times more sensitive than that with H_2O_2.

It is known that the oxidation products of o-tolidine which are formed break down rapidly. Thus, when this reagent is used for determining chloride, the color disappears completely after about five minutes. Under

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* Since the lanthanum nitrate we had at our disposal contained about 0.14% Ce, we had to purify it specially by the method of Klinaev and Senyavin. [12].

TABLE 1

Concentration		Concentration		Concentration	
μg Ce per 100 ml	Optical density	μg Ce per 100 ml	Optical density	μg Ce per 100 ml	Optical density
30	0,040	73	0,095	150	0,190
30	0,038	73	0,093	150	0,190
30	0,038	102	0,132	150	0,188
73	0,092	102	0,133	150	0,195

TABLE 2

Ce taken, μg	Ce found, μg	Error (relative), %
15	14,2	—5,5
15	14,6	—2,8
15	14,0	—6,6
15	14,6	—2,8
60	57	—5,0
120	116	—3,3
150	147	—2,0

TABLE 3

Mineral	Amount of sample taken, g	Ce, %
Apatite	0,5	0,10
»	0,5	0,10
»	0,1	0,11
Titanite	0,1	0,52
»	0,020	0,53
Monzonite	0,5	$2{,}8\cdot 10^{-3}$
»	0,5	$2{,}6\cdot 10^{-3}$

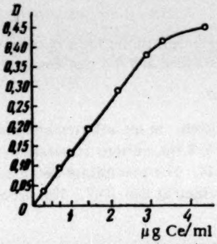

Fig. 1. Calibration curve for determination of cerium by means of o-tolidine.

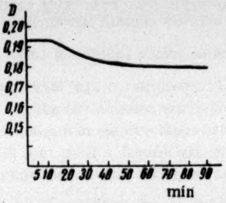

Fig. 2. Relation between optical density and time.

the conditions which we used for our work the yellow color was maintained for hours and only disappeared on the following day. The color was completely stable for 20 minutes after addition of the reagent; subsequently the solution slowly grew pale (Fig. 2). This time is fully sufficient for carrying out photometric measurements. Changes in the pH of the medium from 0 to 4 have no appreciable influence on the sensitivity of the reagent.

When 12 mg of $La(NO_3)_3$ was used as a collector, 10-200 μg of cerium was coprecipitated quantitatively.

As for the reproducibility of the method, which, in the given case will be determined mainly by the completeness of the conversion of Ce^{III} into Ce^{IV} and the stability of the oxidation products of o-tolidine, one can have an estimate of it from the results given in Table 1.

Bearing in mind the use of the method for the determination of cerium in minerals and rocks, we examined the effect of iron, aluminum, manganese, and titanium in amounts corresponding approximately to their content in igneous rocks; viz: Ce : Fe = 1 : 10,000; Ce : Al = 1 : 3000; Ce : Mn = 1 : 350; Ce : Ti = 1 : 100.

Precipitation of the hydroxides from a hot original solution containing 15 μg Ce, 36 mg $La(NO_3)_3$ and the corresponding amount of Fe, Al, Mn, and Ti was carried out with ammonia. On cooling, the precipitate was filtered off and dissolved in hydrochloric acid. This hydrochloric acid solution was evaporated to a volume of 2-3 ml and diluted with 10 ml of water; to this solution was then added 30% H_2O_2 dropwise in order to bind the titanium; 80 ml of a cold, saturated solution of oxalic acid was finally added. The solution was heated for one hour at 80°. The lanthanum oxalate did not precipitate immediately, but only after a definite time interval during which the solution had to be stirred.* The precipitate was filtered on the next day through a filter tube fitted with a sleeve, after which it was calcined at 800°. The oxides obtained were dissolved in hydrochloric acid, 0.1-0.2 g of hydroxylamine hydrochloride was added to reduce Mn^{IV} to Mn^{II}, and the hydroxides precipitated with ammonia in a centrifuge tube, after which the solution plus precipitate were heated for five minutes on a water bath. The precipitate was centrifuged, washed with 2% ammonia containing a small amount of ammonium chloride, and then dissolved in the minimum volume of hydrochloric acid. The oxalates were precipitated with 10 ml of oxalic acid solution. The precipitate was heated for one hour at 80°; it was filtered on the next day and calcined at 800°. Ten drops of hot, concentrated sulfuric acid was added to the oxides obtained, and the whole mixed with a dry glass rod; one ml of the o-tolidine solution was added, the whole mixed again for one minute, the solution was diluted with water and then photometrically measured.**

It is clear from Table 2 that under the conditions described above cerium is almost completely coprecipitated. This means that:

1) Even in the presence of relatively large amounts of iron and aluminum, in all probability, soluble cerium oxalate complexes of these elements are not formed.

2) By precipitating the hydroxides first and then the oxalates, manganese is not coprecipitated in the presence of hydroxylamine hydrochloride.

The fact that a number of elements are not coprecipitated with lanthanum oxalate is also connected with the fact that precipitation is carried out in an acid medium. Thorium, yttrium, neodymium, praseodymium, yterbium, terbium, and samarium do not interfere.

The method suggested has been used for the determination of the cerium content of apatite, titanite, and monzonite (Table 3).

During analysis of monzonite certain elements were precipitated with the oxalate precipitate, but during subsequent treatment with sulfuric acid these elements did not dissolve. In such cases, prior to carrying out photometric measurements, the solutions had to be filtered through a very fine paper filter. Filtration does not affect the optical density of the solutions.

Monzonite contains a large number of microcomponents, interference from which could not be accurately forecast beforehand. Accordingly, to a solution of 0.5 g of the mineral containing 14 μg Ce was added 10 μg of additional cerium. 23.4 μg of Ce was found. This indicates that no cerium is lost during the analysis.

SUMMARY

It has been shown that cerium can be determined fairly selectively and sensitively by means of o-tolidine. Cerium is isolated as its oxalate with lanthanum oxalate as a collector. The oxalates are converted into oxides which are then dissolved in hot concentrated sulfuric acid. The o-tolidine solution is added and the optical density of the yellow solution obtained is measured. The molar extinction coefficient is 9,500.

Cerium can be determined in the presence of thorium and rare earths, and in the presence of large amounts of iron, aluminum, manganese, and titanium.

The method has been used for the determination of cerium in apatite, titanite, and monzonite.

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*Initially, we added 12 mg of lanthanum nitrate. Under these conditions the oxalates did not precipitate at all. Accordingly, in our further experiments we added 36 mg of $La(NO_3)_3$ each time.

**At high cerium contents we diluted the solution to 25, 50, and 100 ml.

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DETERMINATION OF SMALL (10^{-2}-10^{-4}%) AMOUNTS OF THORIUM IN ROCKS BY MEANS OF ARSENAZO II

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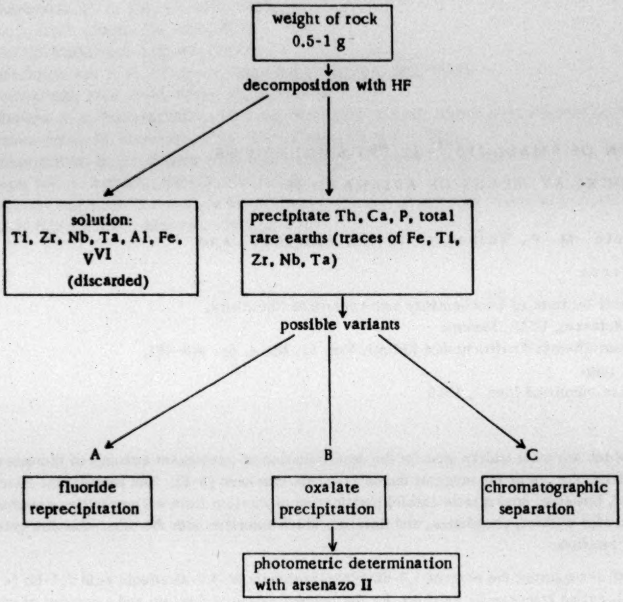
The methods which are most widely used for the determination of microgram amounts of thorium are photometric methods involving the use of the reagents thoron [1-5] and arsenazo [6-8]. The insufficient selectivity of the reagents indicated, however, necessitates careful purification of thorium from accompanying elements such as Zr, Ti, Fe, Al, and also sulfates, phosphates, and fluorides, which interfere with the determination even when present in very small amounts.

Recently, one of us suggested the reagent 1,8-dihydroxynaphthalene-3,6-disulfonic acid 2,7-bis [<-azo-I>-2-phenylarsonic acid], called arsenazo III for short, for the determination of thorium and a number of other elements [9]. This reagent enables thorium to be determined in the presence of large amounts of other elements. The exception is the rare earths, the presence of which in amounts 100-150 times that of thorium cannot be tolerated.

The reagent arsenazo II [10] is the best analog of the well-known reagent arsenazo (uranon) [6]. The synthesis of arsenazo has been described before [11]. Arseanzo II has a number of advantages over arsenazo I as well as over many other reagents which have been suggested for thorium. The most important one is the possibility of determining thorium in fairly acid solutions (0.1-0.6 N HCl), and in the presence of the rare earths, and also in the presence of sulfates, phosphates, and other materials.

In acid solutions arsenazo II reacts with Th, Zr, Ti, U^{IV}, and Fe^{III}, in weakly acid and neutral solutions it reacts with Al, U^{VI}, Cr, Cu, total rare earths, etc. The absorption curve of the reagent and of its compound with thorium is shown in Fig. 1. The selectivity of the determination of thorium with arsenazo II was ensured by choosing a suitable acidity and using masking agents. In a medium of 0.2 N HCl, the influence of almost all the elements is reduced to a minimum, while masking of thorium by phosphates and sulfates is still low. Large amounts of zirconium and titanium interfere, but small amounts can be masked by phosphates specially introduced for this purpose into solution. Two μg of Ti, 3 μg Zr, 4-8 μg Nb and Ta, 5 μg Fe^{III}, 5 μg Cr^{III}, 5 μg Mo, V, and W, 40 μg U^{VI}, 0.5-1 mg Al and 10-150 mg K, Na, Ca, Mg, total rare earths, and Fe^{II} do not interfere with the determination of 10 μg Th. The minimum amount that can be determined is 5-10 μg Th.

In choosing the scheme used for separating thorium, the properties of arsenazo II were borne in mind; these permit determination of thorium in the presence of large amounts of the rare earths and small amounts of zirconium, titanium, niobium, and tantalum. This enabled us to use the simplest scheme. The test material is decomposed by 2-3 evaporations with hydrofluoric acid. During this stage a large part of the zirconium, titanium, niobium, tantalum, aluminum, iron, and uranium (VI) which form soluble fluoride complexes is removed, while the thorium remains in the precipitate together with the rare earths and calcium, which act as carriers for thorium. The scheme chosen for separating the impurities can be represented as follows:


weight of rock
0.5-1 g
decomposition with HF
solution:
Ti, Zr, Nb, Ta, Al, Fe, V^{VI}
(discarded)
precipitate Th, Ca, P, total rare earths (traces of Fe, Ti, Zr, Nb, Ta)
possible variants
A
B
C
fluoride reprecipitation
oxalate precipitation
chromatographic separation
photometric determination with arsenazo II

A. Fluoride Reprecipitation. The fluorides were reprecipitated by the action of hydrofluoric acid on the precipitate of hydroxides obtained after dissolving the first precipitate of fluorides in hydrochloric acid and precipitating with ammonia. The carrier for thorium was the rare earths plus calcium, which are isolated together with thorium from the rock. When the rock only contains a small amount of these elements, an additional 15-20 mg of one of them should be added in order to ensure the fullest possible coprecipitation of thorium. The filtered precipitate of fluorides was dissolved and evaporated several times with concentrated hydrochloric acid in order to remove F^- ions, and, after dissolving the dry residue in HCl (1 : 10) thorium was determined with arsenazo II. A determination takes 6-8 hours.

B. Oxalate Precipitation. After fluoride decomposition of the sample and removal of F^- ions by evaporation with $HCl + HClO_4$, thorium was precipitated homogeneously with the oxalates of the rare earths or calcium using acetonedioxalic acid under the acidity conditions recommended by Kuznetsov and Nikol'skaya [7], and the conditions recommended for calcium by Zaikovskii and Gerkhardt [8]. The oxalates were filtered off, ignited, and the oxides dissolved in HCl (1 : 10), after which thorium was determined photometrically with arsenazo II. The determination takes 24 hours.

C. Chromatographic Separation of the Impurities. Final purification of thorium from impurities after fluoride decomposition was also carried out by means of ion exchange. For this purpose we used the Russian resin KU-2 in the H-form (100 mesh), which sorbs from the 1 N hydrochloric acid solution obtained by dissolving the hydroxides, both thorium and the interfering elements. But their sorption stability is different: zirconium, niobium, tantalum, and titanium are eluted completely with 7 ml of 0.1 N oxalic acid, while thorium is held back on the resin and passes into the eluate on subsequently passing 20-25 ml of a saturated ammonium oxalate solution through the resin. The conditions for the chromatographic separation of thorium and the accompanying impurities are as follows: column diameter, 7 mm; height of resin column 120-130 mm; rate at which the solution is passed through the

TABLE 1

Completeness of Separation of Impurities in Various Analytical Schemes

Separation scheme	Sample						
	1			2			3
	Th : Zr	Th : Ti	Th : (Nb+Ta)	Th : Zr	Th : Ti	Th : (Nb+Ta)	Th : Zr
Ratio in the rock	1 : 126	1 : 309	1 : 21	1 : 111	1 : 80	1 : 15	1 : 400
After fluoride decomposition	1 : 12	1 : 105	1 : 1	1 : 15	1 : 40	1 : 2	1 : 20
After fluoride reprecipitation	1 : 0,25	1 : 0,4	1 : 0,1	1 : 0,0	1 : 0,18	1 : 0,3	—
After fluoride-oxa-oxalate treatment	—	—	—	—	—	—	1 : 0,4
After fluoride-chromatographic separation	—	1 : 0,3	—	1 : 0,2	—	1 : 0,1	—

Note. Control of the degree of separation of the impurities was effected with the help of the radioactive isotopes Zr^{95}, Nb^{95}, Ta^{182} according to their γ-radiation. Titanium was determined by oscillographic polarography.

column 10-12 drops/min. The eluate obtained containing thorium was evaporated to dryness, and the oxalate ions destroyed by boiling with 20 ml concentrated HNO_3. In order to remove NO_3^- ions, the mixture was evaporated three times with hydrochloric acid, and the dry residue obtained then dissolved in HCl (1 : 10), and the thorium determined in the solution obtained photometrically with arsenazo II. The fluoride-chromatographic method takes 12 hours.

In Table 1 are given the ratios of thorium and some of the impurities before and after separation. As is evident from this table, all the methods of separation studied lead to satisfactory ratios of thorium and impurities in the final products.

At the same time completeness of extraction of thorium was checked by means of its radioactive isotope UXI, by measuring the soft β-radiation of UXII found in equilibrium with the former. It was found that the total loss of thorium throughout the whole analytical procedure, whatever separation scheme was used, lies within the limits 12-14%.

Table 2 contains results for the determination of thorium carried out by the three schemes described: sample 1, melanocratic aegirite luyavrite; sample 2, evdialite luyavrite; sample 3, foyaite and evdialite; sample 4, foyaite; sample 5, alaskaite granite; samples 6 and 7, porphyritic syenite; sample 8, pegmatoid syenite; sample 9, foyaite and murmanite. Determination of thorium in monazites has been described previously [12].

As is evident, all three methods using arsenazo II give results in agreement with each other, and also with those of other methods. Accordingly, the decisive choice of the scheme to be used for separating thorium is determined solely by the rapidity and convenience of the operations. We think that two variants can be recommended: a double fluoride and a fluoride-oxalate precipitation.

Double Fluoride Precipitation. 0.5-1 g of finely ground rock is moistened with water in a 150-200 ml platinum basin; it is treated with 10-15 ml of concentrated HF and evaporated to dryness on a sand bath. To the dry residue is added 10-15 ml of HF and the mixture heated on a sand bath to a small volume; it is diluted with 30-40 ml of water and heated for 10-15 minutes. After cooling to room temperature, the fluorides are filtered through a 9 cm "blue band" filter (a polyethylene funnel or an ordinary funnel which has been covered with paraffin is used), and washed first with dilute HF (1 : 20), and then with water which had been used beforehand for washing the platinum basin. The washed precipitate is then washed off the filter paper into the same platinum

TABLE 2

Analysis of Rocks (%)

Method used for determining thorium		Sample									Analysis carried out by:
		1	4	2	5	6	8	7	3	9	
Emanation		$3{,}3\cdot10^{-3}$	$4{,}7\cdot10^{-3}$	$1{,}0\cdot10^{-2}$	—	$3{,}9\cdot10^{-3}$	$6{,}2\cdot10^{-3}$	—	—	—	K. G. Kunasheva (Moscow State University)
Double oxalate precipitation and colorimetric determination of Th with arsenazo I		$4{,}4\cdot10^{-3}$	$4{,}9\cdot10^{-3}$	$8{,}2\cdot10^{-3}$	—	—	—	—	$3{,}8\cdot10^{-3}$	$5{,}2\cdot10^{-3}$	A. I. Polyakov and Yu. A. Balashov (GEOKhI)
Double fluoride precipitation	with arsenazo II	$4{,}1\cdot10^{-3}$	$4{,}7\cdot10^{-3}$	$8{,}0\cdot10^{-3}$	$5{,}4\cdot10^{-3}$	$4{,}8\cdot10^{-3}$	$6{,}9\cdot10^{-3}$	$5{,}7\cdot10^{-3}$	—	—	M. P. Volynets (GEOKhI)
Fluoride-oxalate precipitation		$4{,}1\cdot10^{-3}$	—	$8{,}1\cdot10^{-3}$	$6{,}0\cdot10^{-3}$	$4{,}7\cdot10^{-3}$	$7{,}0\cdot10^{-3}$	$6{,}0\cdot10^{-3}$	$4{,}1\cdot10^{-3}$	$4{,}8\cdot10^{-3}$	Yu. A. Balashov and V. V. Bagreev (GEOKhI)
Fluoride-chromatographic method		$4{,}4\cdot10^{-3}$	—	$7{,}8\cdot10^{-3}$	—	—	—	—	—	—	M. P. Volynets (GEOKhI)

Note. The mean values of 3-6 determinations are given; the deviation between parallel determinations by each of the methods does not usually exceed 10-15%; only in rare instances did it reach 20%.

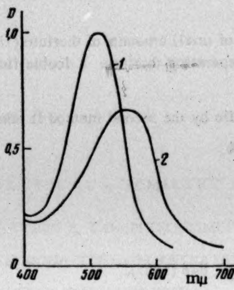


Fig. 1. Absorption curves for a $2.5 \cdot 10^{-5}$M solution of arsenazo II (1) and a $2.5 \cdot 10^{-5}$M solution of the complex of thorium and arsenazo II (2). SF-4 spectrophotometer, 10 mm cuvette.

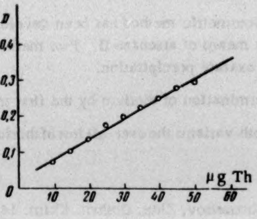


Fig. 2. Calibration curve.

basin, 8-10 ml of concentrated HF is added and the mixture heated until the fluorides have dissolved completely. The solution is evaporated almost to dryness, it is diluted with water and again evaporated to a small volume. After diluting with water to 10-15 ml the hydroxides are precipitated with ammonia; after standing for 15 minutes the hydroxides are filtered off and washed with ammonia water. The washed hydroxides are transferred from the filter paper into the same basin once again and treated with 10-15 ml of concentrated HF. After heating the solution on a sand bath and subsequently cooling it, the fluorides are filtered off as in the first operation, they are washed, and then washed off the filter into a 50 ml beaker. The platinum basin is washed with a total of 15-20 ml of hot concentrated HCl taken in small portions, which are also added to the contents of the beaker. The solution is carefully evaporated on a sand bath, two lots of 2-3 ml of HCl being added. The dry residue is dissolved in 5 ml HCl (1 : 10), and transferred through a moist 5 cm filter paper into a 25 ml standard flask. The beaker is rinsed with water, which is combined with the main solution. Into the standard flask is introduced 10-20 mg of ascorbic acid, 2 ml of a 0.5% solution of $NaH_2PO_4 \cdot 2H_2O$, 5 ml of a 0.1% solution of arsenazo II, and the volume made up to the mark with water. The solution is mixed, and after five minutes its optical density is measured on a FÉK-M photocolorimeter with a red filter, using a 50 ml cuvette. The thorium content is determined from the calibration curve (Fig.2). The reference solution is one containing all the reagents with the exception of thorium.

Fluoride-Oxalate Method. Decomposition of 0.5-1 g of the rock with hydrofluoric acid and separation of the fluoride precipitate is carried out as described above. The fluorides obtained are treated in a platinum basin with a mixture of 1 ml of $HClO_4$ and 0.5 ml HCl while heating on a sand bath. The solution is evaporated to dryness and the dry residue treated twice with 5-10 ml of concentrated HCl, the mixture being evaporated to dryness each time.

When the rare earths are used as the coprecipitant the following analytical procedure is used: the dry residue of chlorides is dissolved in 15 ml of 1.5 N HCl and transferred to a 200 ml beaker, the basin being rinsed with water. A solution containing 20 mg of the rare earths is added, and the volume made up to 100 ml with water. When calcium is used as the coprecipitant the dry residue of chlorides is dissolved in 5.0 ml of 1.5 N HCl, the solution is transferred to a 200 ml beaker and the basin rinsed with water; a solution of calcium chloride containing 40 mg Ca is then added, this is followed by a saturated solution of sodium acetate until the pH is about 5 (congo red), and the volume made up to 100 ml with water. Subsequently, in both cases (rare earths or calcium as the coprecipitant) 15-20 ml of acetonedioxalic acid is added and the solution boiled for 15 minutes; it is finally left overnight. On the following day the precipitate of oxalates is filtered through a "blue band" or a double "white band" filter; it is washed 3-4 times with a 1% solution of oxalic acid; the filter paper plus precipitate is transferred to a porcelain crucible in which they are ignited, and then calcined at 600-700°. The oxides are dissolved in 3-5 ml of concentrated HCl and the solution evaporated to dryness on a water bath. The residue is dissolved in 5 ml HCl (1 : 10) and the solution transferred to a 25 ml standard flask (if the solution is turbid, it is filtered). The conditions used for the subsequent photometric determination have been described in the previous section. The only difference in this case is that 20 mg of the rare earths or 40 mg of Ca are added, respectively, to the zero and standard solutions.

SUMMARY

A photometric method has been developed for the determination of small amounts of thorium (10^{-2}-10^{-4}%) in rocks by means of arsenazo II. Two methods are recommended for separating thorium: a double-fluoride and a fluoride-oxalate precipitation.

Determination of thorium by the first method takes 6-8 hours, while by the second method it takes 24 hours.

In both variants the over-all loss of thorium does not exceed 12-14%.

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*Original Russian pagination. See C. B. translation.

THE ANALYTICAL CHEMISTRY OF THORIUM

COMMUNICATION 2. COMPLEXONOMETRIC DETERMINATION OF THORIUM IN MONAZITE CONCENTRATES AFTER ITS ISOLATION ON KU-2 CATION EXCHANGE RESIN

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The methods used for determining thorium in monazite concentrates are long and difficult. The use of ion exchange enables its determination to be speeded up and simplified considerably. A number of chromatographic methods are known for separating thorium from uranium [1-4], the rare earths [5-8], zirconium and hafnium [9-11]. The ion exchange chromatographic method is used both for monazite sands and for other ores containing thorium. The strongly basic anion exchange resin Amberlite IRA-400 in the SO_4-form is used for separating thorium in monazite sands [8]. Thorium is sorbed by the resin in the form of the sulfate complex. Subsequent desorption of thorium is carried out with 2 N hydrochloric acid. The cation exchange resin IRA-120 and the anion exchange resin Dowex-1 are used for the determination of thorium in lignites [12]. In addition, thorium can be separated from other elements on cellulose and other sorbents [13,14].

In the work described here[*] sorption of thorium from hydrochloric acid solutions on KU-2 cation exchange resin [15] with subsequent complexonometric titration of thorium in the presence of xylenol orange [16], was used.

Thorium is quantitatively sorbed on the cation exchange resin KU-2 from a 35% hydrochloric acid solution (Table 1).

TABLE 1

Completeness of Sorption of Thorium on the Cation Exchange Resin KU-2 as a Function of Hydrochloric Acid Concentration (31.1 mg Th taken)

Hydrochloric acid concentration, % by volume	Th found mg	Th sorbed, %	Hydrochloric acid concentration, % by volume	Th found, mg	Th sorbed, %
5	31,1	99,9	30	31,1	99,9
10	30,9	99,5	35	31,1	99,9
15	31,1	99,9	40	30,7	98,7
20	30,8	99,1	45	30,1	96,7
25	31,1	99,9			

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[*] In a previous paper [17] a description was given of a complexonometric determination of thorium after precipitation of iodates and oxalates by the method of "in situ nascendi" reagents.

TABLE 2

Determination of Thorium in the Presence of Zirconium (30.4 mg Th taken)

Introduced		Th found mg	Absolute error, mg	Introduced		Th found mg	Absolute error, mg
Zr, mg	trihydroxy-glutaric acid, g			Zr, mg	tartaric acid		
4,6	1	30,5	+0,1				
4,6	1	30,4	—0,0	4,6	1	30,5	+0,1
4,6	1	30,4	—0,0	4,6	1	30,5	+0,1
9,3	1	30,4	—0,0				
9,3	1	30,5	+0,1	9,3	1	30,3	—0,2
9,3	1	30,3	—0,1	9,3	1	30,9	+0,5
18,6	1	30,9	+0,5	18,6	1	32,5	+2,1
18,6	1	30,9	+0,5	18,6	1	35,5	+5,1
18,6	2	30,9	+0,5	18,6	2	31,9	+1,5
18,6	2	30,9	+0,5	18,6	2	33,0	+2,6

TABLE 3

Determination of Thorium in Monazite Concentrates by a Complexonometric Method

Monazite concentration	Th found, % (after isolation on a KU-2 resin)	Mean %	Th found % (mean) after ppt. of iodates and oxalates by method of "in nascendi" reagents	Th found, % (mean) by the gravimetric iodate method
O —1	7,42; 7,46; 7,52; 7,42; 7,42; 7,52; 7,48	7,46	7,36	7,40
P —1	6,05; 6,07; 6,11; 6,03; 6,00; 6,11	6,06	6,05	6,13
H —1	7,04; 7,06; 7,10; 7,03; 7,03; 7,01	7,04	7,01	6,92
K —1	5,44; 5,51; 5,42; 5,47; 5,51; 5,40	5,47	5,36	5,40
A	5,25; 5,19; 5,17; 5,19	5,20	—	5,18
B	7,52; 7,52; 7,54; 7,42; 7,46; 7,52	7,49	7,59	7,52

The high acidity enhances the selectivity of the method, since, in most cases, this guarantees that other elements are not sorbed; however, as practice has shown, it is convenient to work with 20% by volume hydrochloric acid. Thorium is desorbed from the resin by means of a 20% solution of ammonium carbonate. It is clear from the elution curve (Fig. 1) that 24 ml of eluant, added in portions of 2-3 ml, is sufficient for complete desorption of 40 mg of thorium.

In addition to thorium, zirconium and small amounts of the rare earths are sorbed on the resin. The rare earths do not interfere with the complexonometric titration of thorium. Zirconium interferes with titration of thorium. Sorption of zirconium can be prevented by complexing it with tartaric or trihydroxyglutaric acid (TAB (Table 2).

As is evident from Table 2, by means of trihydroxyglutaric acid it is possible to eliminate the effect of about 10 mg of zirconium, and by means of tartaric acid about 5 mg of zirconium, during determination of 30 mg Th.

During decomposition of monazite with sulfuric acid, large amounts of phosphate ions pass into solution and these hinder complete sorption of thorium on the resin. As a consequence of this we decided to fuse monazite with sodium peroxide [18]. On leaching the melt with water a considerable part of the phosphorus which separates is removed in the form of readily soluble sodium phosphate, while on dissolving the residue in hydrochloric acid* the remaining phosphoric acid precipitates the zirconium so completely, that only 0.3-1.0 mg of this element remains in the solution prior to the sorption step. This amount of zirconium is completely complexed by tartaric or trihydroxyglutaric acid and does not interfere further with the determination of thorium.

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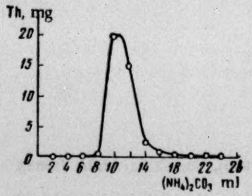
*The phosphate remaining in the residue is sufficient for precipitating zirconium even when the monazite contains about 4% of ZrO_2 (for a monazite sample of 2 g). The small excess of phosphate does not interfere with the sorption of thorium.

Thus, substitution of an acid decomposition by fusion with sodium peroxide not only cuts down the decomposition time (1-2 hours instead of 6-8), but also permits rapid and convenient removal of phosphate and zirconium ions which interfere with thorium determination. As a whole this technique is more rapid and less difficult than the gravimetric oxalate-iodate method, while still maintaining high accuracy.



Curve for the elution of thorium from Ku-2 resin by ammonium carbonate solution.

Method for Determining Thorium. KU-2 resin with particle size 0.3-0.16 mm is washed free from iron with a 20% solution of hydrochloric acid, until the washings give a negative reaction with ammonium thiocyanate. The purified resin is stored under water.

A glass column with a funnel-shaped extension at one end and a ground-glass stopper at the other end is used for the work. The column height is 24 cm, the diameter 1.5 cm. A plug of glass wool is placed on the bottom of the column and 20-25 ml of resin poured on top of it.

The rate at which solution is passed through the column should not exceed 1 ml/ min.

Twograms of monazite concentrate is fused with 10-12 g of sodium peroxide at 600-650° in an iron or corundum crucible. The melt is leached with hot water. The residue is filtered off and washed with a 5% solution of sodium hydroxide. The residue is washed off the folded filter paper with hot hydrochloric acid and 20 ml of water and the precipitate containing zirconium phosphate filtered off. The solution and the wash liquors are collected in a 100 ml standard flask, 5 ml of a 20% solution of trihydroxyglutaric acid or tartaric acid is added, and the volume made up to the mark with water.

A 25 ml aliquot is taken for analysis and passed through the column. As soon as the solution has passed through the column the latter is washed with 70 ml of 20% hydrochloric acid, added in 10-15 ml lots. The final portions of solution issuing from the column should be colorless. 50 ml of a 20% solution of ammonium chloride is then passed through the column. All the solutionsissuing from the column are discarded. Thorium is then desorbed from the column by means of 50 ml of a 20% solution of ammonium carbonate, which is added in 5-7 ml lots. The carbonate solution is collected in a 300 ml beaker. The column is washed with 20-30 ml of water and the solution issuing from the column added to the same beaker. The beaker is covered with a watch glass and hydrochloric acid (1 : 1) added in small amounts until all the ammonium carbonate has been destroyed. The solution is boiled for 2-3 minutes on a hot plate. The watch glass and beaker walls are washed with water. The volume of the solution in the beaker should not exceed 130-150 ml.

The pH of the solution is adjusted to 2.4-2.6 with ammonia using α-dinitrophenol as indicator. For this purpose one or two drops of a 2% alcoholic solution of α-dinitrophenol is added to the solution and the latter neutralized with ammonia (1 : 1) to the appearance of a pale-yellow color, 1-2 drops of hydrochloric acid (1 : 1) is then added.

To the solution with a pH of 2.4-2.6 is added two drops of a 0.5% aqueous solution of xylenol orange, and the solution titrated with about 0.02 sodium ethylenediaminetetraacetate until the raspberry-red color changes to lemon-yellow.

The sodium ethylenediaminetetraacetate is standardized against a standard solution of thorium using the same indicator.

Several samples of monazite concentrates have been analyzed by the method indicated (Table 3).

SUMMARY

A method is suggested for the complexonometric determination of thorium in monazite concentrates in the presence of xylenol orange, after separation of thorium on KU-2 cation exchange resin.

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COMPOUNDS OF QUINQUEVALENT MOLYBDENUM WITH 8-HYDROXYQUINOLINE AND THEIR USE IN ANALYTICAL CHEMISTRY

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Molybdenum in the sexivalent state is quantitatively precipitated by 8-hydroxyquinoline from weakly acid solutions in the form of a greenish-yellow compound whose composition, after washing and drying at 130-140°, corresponds to the formula $MoO_2(C_9H_6NO)_2$. In the form of this compound molybdenum is determined gravimetrically [1-5] and titrimetrically [1, 3] and is separated from a number of accompanying elements [2, 6-9]. A review of the literature is given in Hollingshead's book [10].

Molybdenum in the quinquevalent state also forms compounds with 8-hydroxyquinoline [11]; however, they have not been isolated in the individual state and their composition had not been established.* The possibility has been deomonstrated of separating Mo^V and Mo^{VI} in the form of their compounds with 8-hydroxyquinoline by means of paper chromatography [11].

The aim of the work described here included a systematic study of the interaction of quinquevalent molybdenum with 8-hydroxyquinoline, and a study of the possibility of using the compounds formed in analytical chemistry.

EXPERIMENTAL

Ammonium molybdate solution was prepared by dissolving the commercial preparation in water; the solution obtained was standardized gravimetrically by the 8-hydroxyquinoline method [10]. One ml of the solution was found to contain 1.934, 1.940, 1.928 mg of Mo, an average of 1.934 mg Mo/ ml. This stock solution was diluted ten times.

The salt $(NH_4)_2MoOCl_5$ was synthesized by Klason's method [12].

A hydrazine hydrochloride solution used for reducing sexivalent molybdenum was prepared by dissolving 100 g of $NH_2NH_2 \cdot 2HCl$ in 1000 ml of water.

A 3% solution of 8-hydroxyquinoline was prepared as follows. Three gram of 8-hydroxyquinoline was dissolved in the minimum amount of glacial CH_3COOH, the solution was diluted with water to 100 ml, ammonia was then added dropwise until a faint turbidity appeared, dilute CH_3COOH was finally added to dissolve the turbidity.

Preparation of, and Analysis of the Compounds formed between Quinquevalent Molybdenum and 8-Hydroxyquinoline. Experiments showed that, depending on the conditions

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* Trivalent molybdenum in the form $(NH_4)_2MoCl_5$ forms with 8-hydroxyquinoline at room temperature a black compound which is soluble in acetone; the solution obtained, which is red in color, is unstable on standing, probably as the result of the oxidation of trivalent molybdenum.

TABLE 1

Composition of the Compound of Quinquevalent Molybdenum and 8-Hydroxyquinoline

Preparation No.	Found in the black compound, %								Found in the greenish-yellow compound, %							
	Mo		Mo_2O_3		C_9H_6ON (by difference)		H_2O		Mo		Mo_4O_{10}*		C_9H_7ON (by difference)		H_2O	
1	22,60	22,59	28,26	28,25	69,91	70,10	1,83	1,65	22,58	22,62	31,99	32,05	56,03	56,02	12,00	11,93
2	22,89	22,90	28,63	28,64	57,45	67,38	3,92	3,98	22,59	22,84	32,00	32,36	55,58	55,10	12,42	12,54
3	22,75	22,90	28,45	28,64	70,15	69,88	1,40	1,48	22,95	22,92	32,52	32,47	54,95	55,02	12,51	12,51
4	23,89	24,05	29,88	30,07	67,70	67,72	2,42	2,21	22,52	22,52	31,91	31,91	56,34	56,14	11,75	11,95
Mean	23,07		28,60		68,69		2,36		22,69		32,15		55,78		12,20	

$Mo_2O_3(C_9H_6ON)_4 \cdot H_2O$. Calculated %: 22.99 Mo (or 28.75 Mo_2O_3). 2.16 H_2O and 69.08 C_9H_6ON (black compound)

$H_2Mo_4O_{11}(C_9H_7ON)_7 \cdot 11H_2O$. Calculated %: 21.60 Mo (or 30.61 Mo_4O_{10}). 12.17 H_2O and 57.19 C_9H_7ON (greenish-yellow compound)

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* Calculated in terms of Mo_4O_{10} and not of Mo_4O_{11} since one oxygen atom leaves with water.

used, quinquevalent molybdenum forms with 8 hydroxyquinoline 2 different, sparingly soluble compounds which differ from each other in color and composition.

Precipitation of Quinquevalent Molybdenum at Room Temperature (in weakly acid solution). In this case 8-hydroxyquinoline always gives a precipitate with a greenish-yellow color with quinquevalent molybdenum. In order to prepare it 1 g of $(NH_4)_2MoOCl_5$ was dissolved in 50 ml of water acidified with a few drops of concentrated hydrochloric acid. To the solution obtained was added, with vigorous stirring, 100 ml of a cold 4% solution of 8-hydroxyquinoline in 2 N acetic acid. The greenish-yellow precipitate which separated out was filtered off through a No. 3 or No. 4 glass filter, it was washed first with cold 0.5 N acetic acid several times, and then with cold water, and dried in air to constant weight.

The filtrate had a pH of about 3.

Precipitation of Quinquevalent Molybdenum at the Boiling Point (from weakly acid solution). Under these conditions 8-hydroxyquinoline always forms with quinquevalent molybdenum a black-colored compound with a reddish tinge. One g of $(NH_4)_2MoOCl_5$ was dissolved in 50 ml of water containing a few drops of concentrated hydrochloric acid. The solution was heated to the boil, then while the heating was continued, 100 ml of a hot (60-80°) 4% solution of 8-hydroxyquinoline in 2 N acetic acid was added with vigorous stirring, after which the pH was adjusted to 3.8-4.2. The solution plus the black precipitate was heated for a few more minutes, and the precipitate filtered off through a No. 3 and No. 4 glass crucible, it was washed with hot water and dried in air to constant weight.

In all, four preparations each of the greenish-yellow and black precipitates were synthesized and analyzed. Qualitative tests showed that all the preparations were free from chlorine. The water of crystallization in both molybdenum compounds was determined from the decrease in weight observed on drying the air-dry materials in a drying oven at 130-140° to constant weight (1-2 hours). At 100-105° preparations of the greenish-yellow precipitate did not reach constant weight. On drying the black precipitates (obtained at pH 3.8-4.2) at 130-140° for 1-2 hours, no visible changes were observed. Under the same conditions the greenish-yellow precipitate acquired

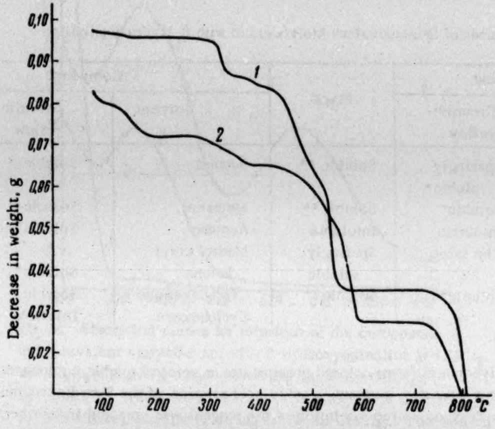

Fig. 1. Thermogravigrams for the compounds of quinquevalent molybdenum with 8-hydroxyquinoline. 1) Black compound; 2) greenish-yellow compound. Obtained on a continuously recording balance. The temperature was raised from 40 to 800° in the course of five hours.

a yellowish-green color. The molybdenum content was determined by the 8-hydroxyquinoline method after oxidizing the molybdenum to the sexivalent state and destroying the organic matter. For this purpose, to an accurately weighed amount of the preparation (0.1-0.2 g) was added 5 ml of a mixture of 1 : 1 concentrated hydrochloric and nitric acids and the whole evaporated almost to dryness on a sand bath. This operation was repeated several times. On completion of the oxidation, 50 ml of water was added to the residue and the solution obtained neutralized until it gave a weakly acid or neutral reaction to methyl red, the solution was then heated to the boil and sexivalent molybdenum precipitated with 8-hydroxyquinoline [10]. The 8-hydroxyquinoline content was determined by difference (satisfactorily coincident results could not be obtained in parallel determinations when an attempt was made to determine 8-hydroxyquinoline by titration with potassium bromate, or on the basis of Kjeldahl determinations of its nitrogen).

The analytical results (Table 1) show that the composition of the black compound is very accurately represented by the formula $Mo_2O_3(C_9H_6ON)_4 \cdot H_2O$. The composition of the greenish-yellow compound differs appreciably from that of the black compound. The greenish-yellow compound approximates in composition to the formula $H_2Mo_4O_{11} \cdot (C_9H_7ON)_7 \cdot 11H_2O$. Although for all four preparations of the greenish-yellow compound synthesized at different times, comparatively close results were obtained during determination of molybdenum and water, one could not be completely sure that these compounds were absolutely pure.

The structure of the black compound of molybdenum can be represented by the formula:

$$(C_9H_6NO)_2=MoO-O-MoO=(C_9H_6NO)_2 \cdot H_2O$$

The formation of two compounds differing in color and composition is apparently related, on the one hand, with the amphoteric character of 8-hydroxyquinoline, which can react both as a weak acid and as a weak base, and on the other hand, with capacity of quinquevalent molybdenum to exist in aqueous solutions in the form of different anions and oxygen-containing cations.*

It should be noted that quinquevalent exhibits a similarity to quinquevalent vanadium, which forms compounds similar in character and yellow and black in color with 8-hydroxyquinoline [10].

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* Sexivalent molybdenum is known to react with 8-hydroxyquinoline as an acid.

TABLE 2

Solubility of the Compounds of Quinquevalent Molybdenum with 8-Hydroxyquinoline

Compound		Black	Compound		Black
Solvent	Greenish-yellow		Solvent	Greenish-yellow	
CCl_4	Sparingly soluble•	Soluble ••	Butanol	Soluble •	Soluble••
$CHCl_3$	Soluble•	Soluble••	Methanol	Soluble•	Soluble ••
$C_2H_5OC_2H_5$	Insoluble	Insoluble	Acetone	Soluble•	Soluble ••
Benzene	The same	Sparingly soluble	Methyl ethyl ketone	Soluble•	Soluble ••
Isoamyl alcohol	Soluble•	Soluble••	Cyclohexanone	Soluble•	Soluble••
			Cyclohexane	Insoluble	Insoluble

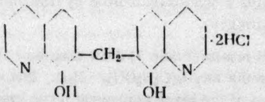
• Yellow-colored solution.

•• Red-colored solution.

Quinquevalent molybdenum forms colored precipitates or colored soluble compounds with various substituted 8-hydroxyquinolines. To a saturated, aqueous, weakly acid solution of the 8-hydroxyquinoline derivative (in the case of 5,7-dibromo-8-hydroxyquinoline a solution of the reagent was prepared in 50% acetone) was added several drops of a 0.2 M solution of $(NH_4)_2MoOCl_5$ and the pH of the solution adjusted with HCl or NaOH using universal indicator paper, and any changes observed. Control tests were carried out in all cases. A solution of 8-hydroxyquinoline-5-sulfonic acid gave with a solution containing quinquevalent molybdenum (yellow color) at room temperature, a soluble compound with an orange color. When an alkali solution was added to the orange-colored solution obtained the molybdenum compound did not hydrolyze. When the weakly acid solution was stood in air for a long time, the orange color changed to intense red. Heating the solution accelerated the appearance of the red color. These qualitative tests showed that quinquevalent molybdenum forms two differently colored soluble complex compounds with 8-hydroxyquinoline-5-sulfonic acid.

5,7-Dibromo-8-hydroxyquinoline gave in weakly acid media (pH 2-3) an orange-colored precipitate. On addition of alkali the precipitate decomposed.

7-Iodo-8-hydroxyquinoline-5-sulfonic acid (ferron) in a weakly acid medium (pH about 2) gave an intensely yellow-orange color with quinquevalent molybdenum. Ferron slowed down the hydrolysis of quinquevalent molybdenum on increasing the pH. The yellow-orange color of the solution (pH 3) did not change on heating.

8,8'-Dihydroxy-5,5'-diquinolmethane hydrochloride, 

precipitated from solutions containing quinquevalent molybdenum, an orange-red amorphous-looking precipitate, when the medium was weakly acid (pH 2-3).

Properties of the Compound of Quinquevalent Molybdenum with 8-Hydroxyquinoline. The black and greenish-yellow compounds of quinquevalent molybdenum obtained at pH 3.8-4.2 and at pH about 3 respectively as indicated above, hardly changed at all on standing for a long time in air (for at least several months) after they had been dried.

On heating to 130-140° for 1-2 hours the black-colored compound did not suffer any visible changes, while the greenish-yellow compound gradually became yellow-green; when the latter was dissolved in chloroform a bright-reddish color was observed. Dilute solutions of the black-colored compound of molybdenum had approximately the same color. This indicates that on heating there occurs partial, slow conversion of the greenish-yellow compound into the black compound. This process was somewhat more rapid when the greenish-yellow compound was allowed to stand in contact with the mother liquor at room temperature, particularly on raising the temperature. The results given above relate to the black compound of Mo^V obtained at pH 3.8-4.2 When the

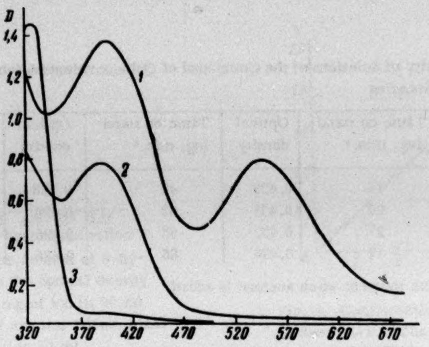


Fig. 2. Absorption curves for solutions of the compounds of quinquevalent molybdenum with 8-hydroxyquinoline in $CHCl_3$. 1) $Mo_2O_3(C_9H_6NO)_4 \cdot H_2O$ (1.733 mg in 25 ml $CHCl_3$); 2) $H_2Mo_4O_{11} \cdot (C_9H_7NO)_7 \cdot 11H_2O$ (1.904 mg in 25 ml $CHCl_4$); 3) 8-hydroxyquinoline (2.61 mg in 25 ml $CHCl_3$). The optical density was measured on a SF-4 spectrophotometer with a layer thickness of one cm, with respect to $CHCl_3$.

black compound was prepared at pH 2.0-3.0 and pH 4.7-5.9, most of it at a temperature of 140° changed into the yellow-green colored compound with a grayish tinge. It is of interest to note that the black precipitate obtained at pH 2.0-3.0 on heating with the mother liquor did not melt, while the black precipitate obtained at pH 4.7-5.9 melted to give a black oily liquid; the latter on cooling solidified to a black dense mass.

All that has been said gives a basis for assuming that under cetain conditions the black-colored compound may partially change into the yellow-green-colored compound and vice versa.

The thermogravigrams (Fig. 1) show that the greenish-yellow and black compounds of quinquevalent molybdenum with 8-hydroxyquinoline, obtained as indicated above (p. 522-524) differ from each other primarily in their water content. On the thermogravigram for the greenish-yellow compound there is a break at 140-160°, which presumably corresponds to the conversion of this compound into the black compound. Above 350° the thermogravigrams for both compounds almost coincide in character. The thermogravigram of the greenish-yellow compound indicates the splitting off of relatively large amounts of water at temperatures below 140°.

The greenish-yellow precipitate dissolved in 2 N NaOH at room temperature; the rate at which it dissolved increased considerably on increasing the NaOH concentration. The black precipitate was almost insoluble even in concentrated NaOH at room temperature, but dissolved on heating to give a green-colored solution, which on heating further changed to a greenish-yellow. The greenish-yellow compound slowly dissolved at room temperature in dilute HNO_3 (2 N) and rapidly dissolved in concentrated HNO_3; on heating this compound was soluble in dilute nitric acid (2 N). The greenish-yellow precipitate dissolved slowly in dilute HCl and H_2SO_4 (2 N) at room temperature, while the black precipitate did not dissolve appreciably in dilute HCl and H_2SO_4 (2 N) at room temperature. Both compounds were readily soluble in concentrated HCl and H_2SO_4 at room temperature and on heating.

The compounds of quinquevalent molybdenum with 8-hydroxyquinoline are soluble in a number of organic solvents and can be extracted by them (Table 2). For the same solvents, almost identical results were obtained with the air-dry preparations and with freshly prepared compounds which had not been removed from the mother liquor.

On adding acetone to an aqueous suspension of the black molybenum compound a red solution was obtained; this was used for the photometric determination of molybdenum (see next page).

TABLE 3

Changes in the Optical Density of Solutions of the Compound of Quinquevalent Molybdenum with 8-Hydroxyquinoline (in 50% acetone) on Standing

Time of standing, min.*	Optical density	Time on standing, min.*	Optical density	Time on standing, min.*	Optical density	Time on standing, min.*	Optical density
5	0.440	16	0.438	42	0.428	110	0.423
6	0.440	20	0.435	63	0.428	145	0.421
9	0.440	27	0.432	68	0.425	167	0.416
13	0.438	37	0.430	85	0.425	178	0.412

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*The time is counted from the moment when acetone is added.

TABLE 4

Determination of Molybdenum in the Presence of Foreign Elements (0.39 mg Mo taken)*

Added, mg	Ratio Mo:Me	Mo, mg		Added, mg	Ratio Mo:Me	Mo, mg	
		found	error			found	error
0,9 Ca($CaCl_2 \cdot 6H_2O$)	1 : 2,2	0,40	+0 01	0,3 Fe($FeCl_3 \cdot 6H_2O$)	1 : 0,7	0,58	+0,19
5,6 Ca($CaCl_2 \cdot 6H_2O$)	1 : 14	0,43	+0,03	0,5 Mn($MnCl_2 \cdot 4H_2O$)	1 : 1,2	0,33	−0,06
0,1 Mg($MgSO_4 \cdot 7H_2O$)	4 : 1	0,41	+0,02	2,7 Mn($MnCl_2 \cdot 4H_2O$)	1 : 6,8	0,31	−0,08
2,4 Mg($MgSO_4 \cdot 7H_2O$)	1 : 6	0,38	−0,01	2,7 Mn($MnCl_2 \cdot 4H_2O$)	1 : 6,8	0,31	−0,08
4,9 Mg($MgSO_4 \cdot 7H_2O$)	1 : 12,5	0,40	+0,01	1,0 Cr($K_2Cr_2O_7$)	1 : 2,5	0.38	−0.01
0,2 Ni($NiSO_4 \cdot 7H_2O$)	2 : 1	0,41	+0,02	2,0 Cr($K_2Cr_2O_7$)	1 : 5	0,37	−0,02
0,6 Ni($NiSO_4 \cdot 7H_2O$)	1 : 1,5	0,36	−0,03	4,0 Cr($K_2Cr_2O_7$) *	1 : 10	—	—
0,4 Ca($CaCl_2 \cdot 2H_2O$)	1 : 1	0,42	+0,03	0,2 Ti(TiO_2)	2 : 1	0,26	−0,13
6,7 Ca($CaCl_2 \cdot 2H_2O$)	1 : 16,8	0,35	−0,04	0,5 Ti(TiO_2)	1 : 1,2	0,31	−0,08
0,3 Zn($ZnSO_4 \cdot 7H_2O$)	1 : 0,7	0,41	+0,02	1,0 Ce[$Ce(SO_4)_2 \cdot 4H_2O$]	1 : 2,5	0,30	−0,09
0,6 Zn($ZnSO_4 \cdot 7H_2O$)	1 : 1,5	0,35	−0,04	0,5 Ce[$Ce(SO_4)_2 \cdot 4H_2O$]	1 : 1,2	0,31	−0,08
0,1 Fe($FeCl_3 \cdot 6H_2O$)	4 : 1	0,39	0,00	0,4 W($Na_2WO_4 \cdot 2H_2O$)	1 : 1	0,19	−0,20
0.2 Fe($FeCl_3 \cdot 6H_2O$)	2 : 1	0,50	+0,11	0,5 W($Na_2WO_4 \cdot 2H_2O$)	1 : 1.2	0,21	−0,18

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*The precipitates which formed did not dissolve completely in water.

The absorption curves of solutions of the two compounds of quinquevalent molybdenum with 8-hydroxyquinoline in chloroform are shown in Fig. 2. The black compound shows two maxima, the first at 397.5 mμ and the second at 550 mμ, while the greenish-yellow compound shows only one maximum at 395 mμ, which almost coincides with the first maximum for the black compound. The optical density of solutions of the black compound in chloroform slowly decreases with time and after 24 hours the color becomes yellow, the solution obtained thereby has only the one absorption maximum at 370 mμ. It is possible that this is connected with the oxidation of the compound of quinquevalent molybdenum with 8-hydroxyquinoline to the 8-hydroxyquinolate of sexivalent molybdenum, (molybdenyl 8-hydroxyquinolate).

The molar absorption coefficients for a solution of the black compound in chloroform are 16500 at 397.5 mμ and 9500 at 550 mμ; the molar absorption coefficient for a solution of the greenish-yellow compound is 18,200 at 395 mμ.

Photometric Determination of Molybdenum

Formation of the black-colored compound of quinquevalent molybdenum with 8-hydroxyquinoline can be used for the photometric determination of molybdenum. The greenish-yellow compound of quinquevalent molybdenum is less suitable for this purpose. The properties of the black molybdenum compound do not permit its use as a gravimetric form.

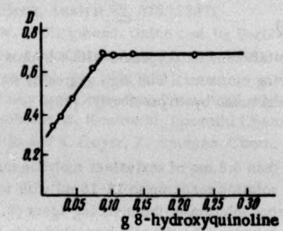

Fig. 3. Effect of the amount of 8-hydroxyquinoline on the optical density of solutions. 0.58 mg of Mo in 20 ml taken and 20 ml of acetone added. Final volume of the solution 50 ml.

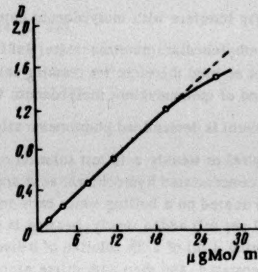

Fig. 4. Conformation of the solutions to Beer's law. (The optical density was measured at 530 mμ).

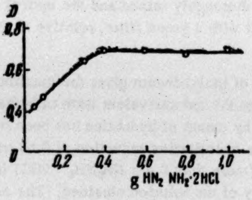

Fig. 5. Effect of the amount of hydrazine hydrochloride on the optical density of solutions of $Mo_2O_3(C_9H_6NO)_4 \cdot H_2O$ 0.58 mg Mo taken (in 13 ml).

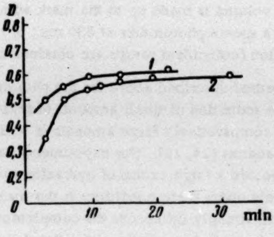

Fig. 6. Duration of heating during reduction of sexivalent molybdenum at various hydrochloric acid concentrations; 1) 2.6 N HCl; 2) 1.3 N HCl.

For the photometric determination of molybdenum, the latter is reduced by means of hydrazine, the quinquevalent molybdenum is then precipitated with 8-hydroxyquinoline from a hot solution at a pH of 3.2-4.2 in the form of $Mo_2O_3(C_9H_6NO)_4 \cdot H_2O$; this precipitate is dissolved, without filtering it, in acetone, and the optical density of the red aqueous-acetone solution obtained measured at 530 mμ .

Experiments showed that in order to get maximum optical density values, it is necessary to heat the solutions on a boiling water bath for more than eight minutes after addition of 8-hydroxyquinoline. More than 0.09 g of 8-hydroxyquinoline in 20 ml must be added to 0.58 mg molybdenum (Fig. 3). The optimum pH of the solution for development of the color lies in the range 3.2-4.2 (the pH was measured by means of a pH-meter with a glass electrode after precipitation of the quinquevalent molybdenum and after cooling the solution to room temperature). The acetone concentration does not affect the color intensity. The color intensity of acetone solutions changes little with time, it is almost stable for three hours (Table 3). Nevertheless, the optical density of the solutions should be measured quickly after dissolving the precipitate in acetone. Ethylenediaminetetracetic acid, oxalic acid, nitrates, and nitrites interfere with the determination; they should be absent. Solutions conform to Beer's law up to 20 μ g Mo /ml (Fig. 4), when the optical density is measured at 530 mμ .

Calcium and magnesium, even in large amounts, do not interfere with molybdenum determination. Cadmium, nickel, and zinc are precipitated by 8-hydroxyquinoline, but their yellow precipitates dissolved in acetone and they do not interfere with molybdenum determination, as long as they are only present in small amounts. Small amounts of iron (less than 0.1 mg) and trivalent chromium (2 mg) do not interfere with molybdenum determination. When large amounts of chromium are present a precipitate is formed which does not dissolve completely in acetone and interferes with the photometric determination. Manganese, copper, cerium, titanium, and tungsten strongly interfere with molybdenum determination (Table 4).

Sodium ethylenediaminetetraacetate (NaEDTA) prevents precipitation of molybdenum with 8-hydroxyquinoline and cannot be used therefore for masking interfering accompanying elements. The high degree of stability of the compound of quinquevalent molybdenum with NaEDTA has been noted by us previously* [13].

Molybdenum is determined photometrically as follows.

To a neutral or weakly acid test solution containing not more than 0.8 mg of sexivalent molybdenum is added 4 ml of concentrated hydrochloric acid and the volume of the solution made up to 13-15 ml with water. The solution is heated on a boiling water bath and 5-7 ml of an aqueous solution of the reducing agent (0.1 g $NH_2NH_2 \cdot 2HCl$ per ml) added slowly, heating is continued for 10-20 minutes. To the still-hot solution is then added with stirring 4 ml of a 3% solution of 8-hydroxyquinoline in dilute acetic acid, and the solution neutralized first with concentrated, and then with dilute ammonia until the appearance of the 8-hydroxyquinolate precipitate. Two ml of an acetate buffer solution with pH 4 is then added and heating continued for 10-15 minutes on a boiling water bath. After cooling to room temperature, the solution plus the precipitate of $Mo_2O_3(C_9H_6ON)_4 \cdot H_2O$ is quantitatively transferred to a 50 ml standard flask. The beaker is washed with 25 ml of acetone (if, during this stage of white precipitate is formed in the beaker, the precipitate can be dissolved by adding a few drops of water). The volume is made up to the mark with water, the whole is thoroughly mixed and the optical density measured on a spectrophotometer at 530 mμ, or on a photocolorimeter with a green filter, relative to water or a blank solution (coincident results are obtained in both cases).

The method described above for the photometric determination of molybdenum gives the maximum conditions for the reduction of small amounts of sexivalent molybdenum to the quinquevalent state of hydrazine. Reduction of comparatively large amounts of sexivalent molybdenum by means of hydrazine has been studied by a number of authors [14, 15]. Our experiments have shown that for the quantitative reduction of 0.58 mg Mo it is necessary to add a large excess of hydrazine hydrochloride (Fig. 5) (more than 0.4 g $NH_2NH_2 \cdot 2HCl$ in 13 ml of water). Only under these conditions is the maximum optical density of the solution obtained. The acidity of the solutions strongly influences the completeness of reduction of sexivalent molybdenum, at low acidity molybdenum blue is formed; in a medium of 1.3-2.6 N HCl, after addition of 0.7 g of $NH_2NH_2 \cdot 2HCl$ to 20 ml of the hot solution, first of all a strong blue color appears, but on further heating on a boiling water bath the blue color disappears. In this case it is necessary to heat for more than 10 min at 2.6 N HCl or for more than 15 min at 1.3 N HCl, in order to ensure complete reduction of sexivalent molybdenum (Fig. 6). On increasing the acidity further, the time to effect reduction is cut down appreciably, but so much acid is introduced into the solution thereby that the subsequent procedure is complicated.

SUMMARY

Quinquevalent molybdenum forms two compounds with 8-hydroxyquinoline; at room temperature a greenish-yellow precipitate is formed, while from a hot boiling solution a black precipitate is formed. The composition of the latter corresponds accurately to the formula $Mo_2O_3(C_9H_6NO)_4 \cdot H_2O$. The composition of the greenish-yellow compound corresponds approximately to the formula $H_2Mo_4O_{11} \cdot (C_9H_7ON)_7 \cdot 11H_2O$. The various properties of the two compounds have been studied, and it has been shown that the black compound of quinquevalent molybdenum can be used for the photometric determination of small amounts of molybdenum (some tenth parts of μg/ml) in a medium of 50% acetone. The method gives accurate results. Ca, Mg, Cd, Ni, and Zn do not interfere, while small amounts of Fe^{III} and Cr^{III} do not interfere either. The method is, however, not very selective.

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CHEMICOSPECTROGRAPHIC QUANTITATIVE DETERMINATION OF SMALL AMOUNTS OF MOLYBDENUM AND TUNGSTEN IN IGNEOUS ROCKS

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The sensitivity of the spectrographic determination of tungsten is relatively low. It never exceeds a value of $5 \cdot 10^{-4}\%$ [1], while in most cases it is significantly lower: 10^{-2}-$10^{-3}\%$ [2-5]. The sensitivity of the spectrographic determination of molybdenum is somewhat higher, about $10^{-4}\%$ [5, 6-8]. Accordingly, during studies of rocks, the molybdenum and tungsten content of which usually varies in the range 10^{-6} to $10^{-3}\%$ [9], direct use of the spectrographic method is only possible after concentrating these elements. A number of papers have been published in which, for the determination of W and Mo in rocks, preliminary chemical enrichment was used [10-14]. Wilson and Fields [13] determined tungsten in rocks after decomposition of the latter with acids. Tungsten was precipitated at the same time as titanium from solution by a mixture of tannin, antipyrine, and cinchonine. The tungsten content of the concentrate thereby obtained was determined spectrographically. The sensitivity of their method was $7 \cdot 10^{-5}\%$. Scobler [14] during the determination of W in ores and concentrates carried out chemical enrichment by means of aluminum hydroxide. The sensitivity of the determination of tungsten in this case was about $2 \cdot 10^{-5}\%$.

The aim of the work described here was to develop a method for the simultaneous determination of tungsten and molybdenum in rocks with a sensitivity of about $n \cdot 10^{-5}$ for W and $n \cdot 10^{-6}$ for Mo, and with an accuracy of about 10%. Tungsten and molybdenum were determined spectrographically after their chemical enrichment. Igneous rocks of various alkalinity were studied, they varied from ultrabasic to acid and included: dunite, basalt, diorite, granite, etc. Their average composition can be characterized by the figures given in Table 1.

TABLE 1

Average Chemical Composition of the Main Types of Igneous Rocks (According to Luchitskii [15])

Rock	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2
Dunite	40,5	0,86	8,38	46,32	0,70	0,10	0,04	0,02
Basalt	48,24	17,88	9,11	7,51	10,99	2,55	0,89	0,97
Diorite	58,9	16,47	6,93	3,57	6,17	3,46	2,11	0,76
Granite	70,18	14,47	3,35	0,88	1,99	3,48	4,46	0,39

Concentration of the test elements from the rocks was effected by means of methyl violet and tannin [15, 16]. Using the radioactive isotopes Mo^{99} and W^{185} it was established that a mixture of these reagents quantitatively precipitates tungsten and molybdenum from very dilute solutions.

TABLE 2

Checking the Technique for the Chemicospectrographic Determination of W and Mo on Synthetic Mixtures

Added, %		Found, %	
W	Mo	W	Mo
$9,8\cdot10^{-5}$ (G)	$6,4\cdot10^{-4}$ (D)	$1,1\cdot10^{-4}$	$6,9\cdot10^{-4}$
$1,23\cdot10^{-4}$ (D)	$1,9\cdot10^{-4}$ (G)	$1,3\cdot10^{-4}$	$2,1\cdot10^{-4}$
$1,48\cdot10^{-4}$ (G)	$5,5\cdot10^{-4}$ (D)	$1,3\cdot10^{-5}$	$5\cdot10^{-4}$
$1,73\cdot10^{-4}$ (D)	$2,4\cdot10^{-4}$ (G)	$1,5\cdot10^{-4}$	$2,6\cdot10^{-4}$
$2,1\cdot10^{-4}$ (G)	$5\cdot10^{-4}$ (D)	$2,2\cdot10^{-4}$	$4\cdot10^{-4}$
$5,5\cdot10^{-4}$ (G)	$1,05\cdot10^{-4}$ (D)	$4,5\cdot10^{-4}$	$9\cdot10^{-5}$
$8,7\cdot10^{-4}$ (G)	$5,5\cdot10^{-5}$ (D)	$7,2\cdot10^{-4}$	$4,2\cdot10^{-5}$

Note. The letters designate the base to which the test elements were added (G – granite, D – dunite).

TABLE 3

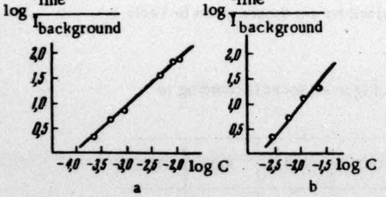
Comparison of the Results of Mo and W Determinations in Rocks

W content, %		Mo content, %	
Direct spectrographic method in which AgCl is added	Chemicospectrographic method	Direct spectrographic method [19]	Chemicospectrographic method
$3,5\cdot10^{-4}$	$3,22\cdot10^{-4}$	$1,4\cdot10^{-4}$	$1,2\cdot10^{-4}$
$1,9\cdot10^{-4}$	$2,3\cdot10^{-4}$	$1,8\cdot10^{-4}$	$1,7\cdot10^{-4}$
$2,6\cdot10^{-4}$	$2,8\cdot10^{-4}$	$2,3\cdot10^{-4}$	$2,3\cdot10^{-4}$
$2,3\cdot10^{-4}$	$3,3\cdot10^{-4}$	$1,1\cdot10^{-4}$	$0,7\cdot10^{-4}$
		$4,5\cdot10^{-4}$	$3,91\cdot10^{-4}$
		$2,8\cdot10^{-4}$	$3,2\cdot10^{-4}$

TABLE 4

Comparison of the Results of the Determination of Molybdenum in Granites, Obtained by Spectrographic and Polarographic Methods

Rock sample	Mo found, %	
	Spectrographic method	Polarographic method
T-1	$2,3\cdot10^{-3}$	$2,7\cdot10^{-3}$
T-2	$6,3\cdot10^{-4}$	$7,3\cdot10^{-4}$
T-3	$1,6\cdot10^{-3}$	$1,8\cdot10^{-3}$
T-4	$3,4\cdot10^{-4}$	$3,1\cdot10^{-4}$
T-5	$2,3\cdot10^{-4}$	$2,8\cdot10^{-4}$
T-6	$2\cdot10^{-4}$	$2,5\cdot10^{-4}$
T-7	$2,2\cdot10^{-4}$	$2,5\cdot10^{-4}$
T-8	$1\cdot10^{-4}$	$0,95\cdot10^{-4}$



Calibration curves for determination of Mo (a) and W (b).

Concentration of W and Mo. One gram of well-ground ore was mixed with 8 g of sodium carbonate* and placed in a platinum crucible. The mixture was then fused on a blowtorch.

Fusion of acid and average rocks was complete in 45 minutes, while for basic and ultrabasic rocks 1 hour 30 minutes was necessary. The melt obtained was transferred to a glass beaker. 150 ml of cold water was added and the whole left to stand overnight. The residue was then filtered and carefully washed with 1% sodium carbonate solution (about 150 ml).

To the filtrate, which contains soluble W and Mo salts, was added 2 N HCl until it gave a neutral reaction to methyl orange, 6 N HCl was then added until the pH was 0.18-0.2. To this acidified filtrate was next added 2% solutions of methyl violet and tannin, on the basis of 50 mg tannin and 100 mg of methyl violet per 100 ml of solution, and the final solution allowed to stand for 20-30 minutes to ensure complete coprecipitation of tungsten and molybdenum. The precipitate was then filtered off, dried, and ashed at 600°. The ashed residue was weighed and diluted with a silicate base which had been checked for freedom from Mo and W.

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* The sodium carbonate used for the analysis was recrystallized twice in order to remove traces of molybdenum.

It was established by means of radioactive indicators that the scheme adopted ensures quantitative coprecipitation of W and Mo for contents of the elements in the rock of the order of 10^{-4} and 10^{-5}%, respectively.

Spectrographic Determination of Molybdenum in the ashed concentrate was carried out on a QU-24 quartz spectrograph in a dc arc. Complete evaporation of samples from the canal of a carbon electrode was used. The conditions used for photographing the spectra were as follows: electrodes, carbon with a crater 2.5 mm deep and an opening with a diameter of 3.5 mm. The spectrograph slit was 0.02 mm. The current was 10 amp. The exposure time was 2.5 min. The sample weight was 10 mg. The sample was a mixture of the residue obtained after chemical enrichment of the rock (about 2 mg) with a silicate base (about 18 mg). The spectra were photographed on a "spectrographic type II" plates with a sensitivity of 8 or 11 GOST units.

The line Mo I 3170.35 was used for carrying out the analysis.

Spectrographic Determination of Tungsten in the test residues was carried out on a ISP-51 A spectrograph with a UF-85 camera. The excitation source was a dc arc. The 4294.6 line was used for analysis. The time for complete evaporation and the other conditions were the same as those used for molybdenum determination. "Spectrographic Type II" plates with a sensitivity of 22 GOST units were used for recording the spectra.

The calibration curves for determining Mo and W were constructed on the basis of the three-standards method within the coordinates log R and log C, where R is the relative intensity of the test lines with respect to the background, while C is the concentration of the test elements expressed in % (Fig.). The standards which were used for constructing the calibration curves for Mo and W were prepared using the same silicate base for dilution as that used for the samples. Molybdenum and tungsten were added to the base in the form of MoO_3 and WO_3; the content of Mo and W in the standards was varied from $5 \cdot 10^{-5}$ to $3 \cdot 10^{-1}$%.

The sensitivity of the chemicospectrographic method developed for the determination of molybdenum and tungsten proved to be $2 \cdot 10^{-6}$% and $3 \cdot 10^{-5}$%, respectively.

The reproducibility of the method was checked by taking 15 photographs of the same sample; the mean arithmetic error calculated on the basis of the results obtained proved to be ± 10% of Mo and ± 8% for W.

The precision of the method and the degree of reliability of the results obtained are evident from the results given in Table 2. For high content of the test elements, the results of the chemicospectrographic method were compared with the results obtained for tungsten and molybdenum by a direct spectrographic analysis and by a polarographic method [18] (Tables 3 and 4). Molybdenum and tungsten in the form of their oxides were added to two bases—granite and dunite — in known concentrations; the Mo and W contents were then determined by the chemicospectrographic method. The results were found to be independent of changes in the chemical composition of the rocks and are completely satisfactory. For Mo and W contents greater than 10^{-4}, the determination can be carried out by the spectrographic method without preliminary chemical enrichment. In these cases silver chloride was added for the determination of tungsten in rocks by the spectrographic method. For this purpose the sample was mixed with silver chloride in the proportion of 1 : 1 and the mixture placed in the carbon electrodes, which had an opening with a depth of 4 mm. The excitation source was a 10 amp dc arc. It was established that under these conditions tungsten burns up completely in 60 seconds when the electrode containing the sample was used as the anode. Tungsten was determined on an ISP-51A spectrograph with an UF-85 camera. The line W-I 4294 was used. The spectra were photographed on "Spectrographic Type II" plates with a sensitivity of 22 GOST units.

We succeeded in taking down the sensitivity of the determination of tungsten to a value of $2 \cdot 10^{-4}$%, by taking photographs of three electrodes containing test mixture for 60 sec on the same place on the plate. The deviation between the results obtained by the method did not exceed ± 8.5%.

Results for the W and Mo contents of rocks, obtained by the direct spectrographic method, as well as the analytical results obtained for these rocks by a polarographic method, are compared with the results of the chemicospectrographic method in Tables 3 and 4.

The mean arithmetic error for the chemicospectrographic method does not exceed ± 12-15%. The method developed has been used for the systematic study of the Mo and W content of igneous rocks, for determining the

Mo/W ratio in them and finding the mean content of these elements in the earth's crust.

In conclusion I should like to thank É. E. Vainshtein for valuable advice and L. V. Meshcheryakova for help in carrying out the analysis.

SUMMARY

A method is suggested for the quantitative determination of small concentrations of Mo and W in various rocks. When the concentration of these elements is higher than 10^{-4}%, the rocks can be analyzed by a direct spectrographic method. Rocks containing less than 10^{-4}% of Mo and W are analyzed after preliminary chemical enrichment by means of organic coprecipitants. The concentrates obtained are analyzed spectrographically. The sensitivity of the chemicospectrographic method developed for the determination of Mo and W is $2 \cdot 10^{-6}$% and $3 \cdot 10^{-5}$%, respectively.

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PHOTOMETRIC DETERMINATION OF PALLADIUM IN PRODUCTS FROM NICKEL PRODUCTION

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"Severonickel" Combine

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Compounds of diantipyrylmethane with complex anions of metals are used for the photometric determination of cobalt and iron, and for the gravimetric determination of cadmium [1, 2].

Sudo [3] has established that on adding a solution of antipyrine and excess potassium iodide solution to an acid solution of palladium chloride, a complex compound is formed which is extracted with chloroform. By measuring the optical density of the extract obtained at 340 mμ, it is possible to determine 1-20 μg palladium. Sudo noted that a compound of palladium iodide and antipyrine is thereby formed. The composition of the compound has not been studied.

Our experiments have shown that analogous results can be obtained by adding a solution of diantipyrylmethane instead of antipyrine to a solution of the complex iodide of palladium.

When diantipyrylmethane is used, the compound $(C_{23}H_{24}O_2N_4)_2 \cdot H_2[PdI_4]$ is probably formed, this compound is of undoubted interest for analytical purposes.

For preparing the palladium chloride solution, palladium dimethylglyoximate obtained during the gravimetric determination of palladium was calcined in a muffle furnace, the oxides obtained were reduced with formic acid and the palladium metal obtained dissolved in aqua regia. The solution obtained was evaporated three times with hydrochloric acid. The palladium concentration of the solution was determined gravimetrically. Both the stock and working solutions contained a large amount of hydrochloric acid. The concentration of the working solution was 0.01 mg Pd/ml.

A 2% solution of diantipyrylmethane was prepared by dissolving an aliquot in 0.5 N hydrochloric acid.

A 40% potassium iodide solution was prepared by dissolving chemically pure potassium iodide. The potassium iodide solution should be colorless.

The solutions of the compound of palladium with iodide and diantipyrylmethane in chloroform are cherry-red in color and conform to Beer's law (Fig. 1). On measuring the optical density on a FÉK-M apparatus fitted with a blue filter, it was found possible to determine more than 0.48 μgPd/ml when the layer thickness in the cuvette was 10 mm. The absorption maximum is found at 450 mμ.

Preparation of the colored compound of palladium with iodide and diantipyrylmethane should be carried out in hydrochloric acid media in the absence of oxidizing agents (nitric acid, dilute aqua regia), otherwise elemental iodine separates out, which leads to difficulties.

We have established that an exchange reaction occurs between a solution of palladium dimethylglyoximate in chloroform and aqueous solutions of diantipyrylmethane and iodide, as a result of which a compound of palladium with iodide and diantipyrylmethane is formed in the chloroform layer, while the dimethylglyoxime passes

TABLE 1

Nickel g	Pd intrd. μg	Pd found μg	Copper g	Pd intrd. μg	Pd found μg	Cobalt g	Pd intrd. μg	Pd found μg	Iron g	Pd intrd. μg	Pd found μg	Platinum μg	Pd intrd. μg	Pd found μg	Gold μg	Pd intrd. μg	Pd found μg
0,5	120	120	0,5	48	51	0,5	60	55	0,1	120	119				100	100	100
															100	100	100
															200	100	100
						0,5	100	100									
1,0	48	52	0,5	96	102												
1,0	72	72	0,5	144	150							100	100	100			
1,0	96	96				1,0	48	42	0,4	120	117	120	100	100			
1,0	120	120							1,0	120	81	140	100	100			
1,0	144	144										180	100	100			
						1,0	96	96				200	100	100			
			1,0	60	60												
						1,0	144	144									
									2,0*	100	101						
									2,0*	100	105						
			1,0	48	48												
			1,0	156	156												

Note 1. Solutions of nickel, copper, and cobalt salts were prepared from pure metals. 2. The iron salt solution was prepared from commercial iron sulfate.

* $CuSO_4$ solution was added, and the palladium separated with copper by means of sodium thiosulfate.

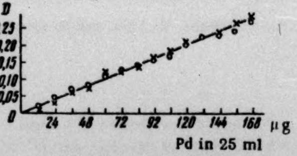

Fig. 1. Calibration curve for the determination of palladium by means of diantipyrylmethane and potassium iodide. ○) Pd, with extraction of dimethylglyoxime; x) Pd, without extraction of dimethylglyoxime.

into the aqueous layer. For the same palladium concentration, the optical density of chloroform solutions of the compound of diantipyrylmethane is considerably greater than the optical density of solutions of palladium dimethylglyoximate. The identity of the compound of palladium with diantipyrylmethane and iodide obtained by the exchange reaction, and by mixing the corresponding compounds, is confirmed by the fact that the absorption curves coincide.

That the dimethylglyoxime does, in fact, pass into the aqueous phase during the exchange reaction was confirmed by the following experiment: dry palladium dimethylglyoximate was suspended in chloroform, and to this suspension was added solutions of diantipyrylmethane and potassium iodide. After shaking for a long time the chloroform layer acquired a dark-cherry color in transmitted light and almost a black color in reflected light. All the palladium dimethylglyoximate dissolved. Dimethylglyoxime was detected in the aqueous phase by the reaction with a nickel salt.

Copper and iron interfere during the direct photometric determination of palladium by means of diantipyrylmethane and potassium iodide as a result of iodine liberation. Accordingly, it is expedient at the beginning to separate palladium in the form of its dimethylglyoximate by extraction with chloroform, and, subsequently, by means of the exchange reaction prepare the compound of palladium with diantipyrylmethane and iodide in the organic phase.

Table 1 contains the results of experiments on the extraction of palladium in the presence of various metals by extraction of palladium dimethylglyoximate with chloroform. They conform to published

TABLE 2

Test material	Found, %		Test material	Found, %	
	Photometrically	Gravimetrically*		Photometrically	Gravimetrically*
Black copper	0,0014	0,0013	Sludge	0,21	0,20
Magnetic fraction	0,019	0,019	»	0,16	0,14
			»	0,19	0,18
Beads from the magnetic fraction	0,026	0,026	»	0,15	0,13
Tailings	0,017	0,016	»	0,16	0,14
»	0,014	0,013	Nickel	0,0054	0,0059
»	0,022	0,025	Sludge**	0,14	0,14
»	0,039	0,044	»	0,13	0,13
»	0,014	0,014	»	0,18	0,19
»	0,027	0,024	»	0,15	0,14
»	0,036	0,033	»	0,13	0,12
»	0,12	0,13	»	0,20	0,21
»	0,058	0,052	»	0,26	0,28

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* Weighed in the form of palladium dimethylglyoxima te.

** Found by means of nitroso-R-salt.

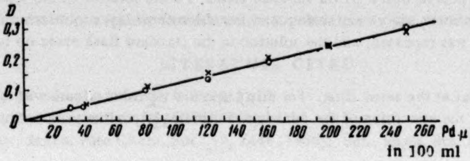

Fig. 2. Calibration curve for palladium determination by means of nitroso-R-salt. ○) Pd, with extraction of dimethylglyoxime; ×) Pd, without extraction of dimethylglyoxime.

results [4] on the possibility of separating palladium from Ni, Cu, Co, Fe, Pt, and Au in this way. All the experiments, with the exception of the extraction of Pd in the presence of large amounts of iron, were carried out as follows: a solution of the salt being tested and a standard solution of palladium chloride were introduced into a 250 ml separating funnel, and the solution diluted to 100 ml with water. Three ml of concentrated hydrochloric acid and 10 ml of a 1% alcoholic solution of dimethylglyoxime were then added and the whole carefully mixed. The mixture was allowed to stand for 15 minutes with periodical shaking.

Palladium dimethylglyoximate was extracted by means of two lots of chloroform (10 and 5 ml) by vigorous shaking, two minutes for both extractions. In order to remove the metal salt, the chloroform solution was washed in in a separating funnel with 25 ml of 0.2 N hydrochloric acid, and the palladium then determined as described below (colorimetrically in the form of palladium diantipyrylmethanate).

The results for solutions containing more than 0.5 g iron per 100 ml were low. In such cases, in order to separate palladium from iron, cupric sulfate was added to the solution and the palladium separated together with copper by means of sodium thiosulfate [5, 6] (see also the analytical procedure).

Palladium Can be Determined Photometrically by Means of Nitroso-R-Salt. On heating with nitroso-R-salt, palladium chloride forms an intensely red-colored compound. When a FÉK-M apparatus fitted with a green filter and a cuvette with a layer thickness of 10 mm were used, the sensitivity for the determination of palladium was 0.30 μg Pd/ml. The optical density of solutions of the compound formed do not change over a wide acidity range from pH 5.57 (acetate buffer) to 0.1 N HCl and 0.05 N HNO_3. The solutions conform to Beer's law (Fig. 2). The colored compound breaks down on boiling with concentrated HNO_3 (5 ml of concentrated HNO_3 per 30 ml solution).

We used nitroso-R-salt for determining palladium, after its removal from accompanying metals, in products from nickel production (Table 2).

The results of the photometric and gravimetric determinations coincide satisfactorily with each other. The advantage of the photometric method is the speed with which it can be carried out and its high sensitivity.

Determination of 0.01-0.05% Palladium in Tailings Containing up to 45% Nickel, 20% Copper, and 5% Iron. To 0.5 g of tailings was added 30 ml of aqua regia and the whole heated; it was then evaporated almost to dryness; it was next treated twice with concentrated hydrochloric acid and evaporated until a moist residue was obtained. The salts were dissolved in water and the residue filtered off and washed with hot water. The insoluble residue plus the filter were calcined and fused with potassium pyrosulfate; the melt was leached with water and the solution combined with the main solution. When the total volume of the solution obtained in this way was more than 100 ml it was evaporated. The solution was transferred to a 250 ml separating funnel, 3 ml of concentrated hydrochloric acid and 10 ml of a 1% alcoholic solution of dimethylglyoxime were added and the whole vigorously mixed and left to stand for 15 minutes. Ten ml of chloroform was added and the mixture shaken for two minutes. The chloroform layer was poured off into another separating funnel.

The extraction was repeated with 5 ml of chloroform and the chloroform layer combined with the previous lot. The chloroform was extracted 2-3 times with 25 ml of 0.2 N hydrochloric acid. The wash liquor was discarded. To the washed chloroform extract was added 10 ml of a 40% potassium iodide solution and 20 ml of a 2% solution of diantipyrylmethane in 0.5 N hydrochloric acid. The whole was shaken vigorously for two minutes. During this stage the white precipitate which separates out on adding the reagents should dissolve completely.

The chloroform layer was poured into a 25 ml standard flask. To the solution in the separating funnel was added 2 ml of chloroform, the mixture vigorously shaken and the chloroform layer transferred into the standard flask. Washing with chloroform was repeated, and the solution in the standard flask made up to the mark with chloroform.

A blank test was carried out at the same time. For this purpose a separate aliquot was taken through the whole analytical procedure with the exception of the addition of dimethylglyoxime prior to the chloroform extraction.

Determination of Less than 0.01% Palladium in Products Containing Large Amounts of Iron. An aliquot, the amount of which depended on the expected palladium content, was dissolved on heating in aqua regia. The solution was evaporated until moist salts were obtained; 10-20 ml of sulfuric acid (1 : 1) was added. The solution was then evaporated to the appearance of white fumes. The residue was dissolved in water on heating and the insoluble part filtered off. The calcined insoluble residue was fused with potassium pyrosulfate. The melt was leached with water and the solution obtained added to the main solution.

To the solution obtained, sulfuric acid (1 : 1) was added at the rate of 19 ml of acid per 100 ml of solution. The solution was heated to the boil and a 20% solution of sodium thiosulfate added until all the copper had been precipitated. When the samples being analyzed do not contain copper, a solution of copper sulfate is added prior to precipitation with sodium thiosulfate. After complete coagulation, the precipitate was filtered off and calcined in a muffle furnace.

In order to reduce the palladium oxides, the calcined residue was treated on moderate heating with formic acid and the solution evaporated to dryness. The residue was dissolved in aqua regia contained in a No. 6 porcelain crucible, and the mixture evaporated until damp salts were obtained; the residue obtained was dissolved in hydrochloric acid and the solution again evaporated until the damp salts were obtained. The salts were dissolved in water and transferred to a separating funnel. All the remaining operations were carried out as described above for the analysis of tailings.

A blank test was carried out with a separate aliquot, all the same operations being repeated except that no dimethylglyoxime was added prior to extraction with chloroform.

A calibration curve was constructed on the basis of 15 points corresponding to 1 to 15 ml of a solution (1 ml of solution contained 10 μg Pd). To the solution of palladium chloride in a 250 ml separating funnel was added 3 ml of concentrated hydrochloric acid and 10 ml of a 1% alcoholic solution of dimethylglyoxime, the solution was diluted to 100 ml with water and all the operations described above for the analysis of palladium carried out.

Photometric Determination of Palladium by Means of Nitroso-R-Salt. All the operations described above were the same with the exception that palladium was extracted with chloroform in the form of its dimethylglyoximate. The chloroform solution of palladium dimethylglyoximate was evaporated to dryness on a water bath. The dimethylglyoxime was destroyed by heating the dry residue with 25 ml of aqua regia. The solution was evaporated to dryness, 10 ml of concentrated hydrochloric acid was added and the solution evaporated until the moist salts were obtained. The chlorides were dissolved on heating in water, 10 ml of a 0.1% solution of nitroso-R-salt was added and the solution heated to the boil; the solution was then cooled and transferred to a 100 ml standard flask. The solution was diluted to the mark with water and the optical density measured on a FÉK-M apparatus fitted with a green filter.

The control solution was prepared from the reagents used.

In order to construct a calibration curve, 10 ml of a 1% alcoholic solution of dimethylglyoxime was added to measured amounts of the standard palladium chloride solution, and all the operations described above carried out.

SUMMARY

It has been shown that an exchange reaction occurs between solutions of palladium dimethylglyoximate in chloroform and aqueous solutions of diantipyrylmethane and potassium iodide, as a result of which a compound of palladium with iodide and diantipyrylmethane is formed in the chloroform solution.

It has been found that nitroso-R-salt gives a colored compound with palladium chloride solutions, and that this compound is suitable for the colorimetric determination of palladium.

Methods have been developed for the determination of palladium in the products of nickel production.

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SPECTROPHOTOMETRIC STUDY OF THE REACTION BETWEEN TRIVALENT IRON IONS AND DIMETHYLGLYOXIME

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Studies of the dioximate complexes of metals were started as the result of the classical work of Chugaev [1]. Dimethylglyoxime reacts with metal salts, mainly salts of elements of the eighth group of the periodic system, including iron. Ferrous ions form several complexes with dimethylglyoxime, the composition of these complexes varying with the pH of the medium. In the pH range 5-6.5 a complex cation of the composition $Fe(HDm)^+$ is formed, while in the pH range 6.5-11 $Fe(HDm)_2$ predominates, and, in even more alkaline media, dimethylglyoxime forms a complex with the composition FeDm [2] with ferrous iron.

The interaction of ferric iron with dimethylglyoxime has not yet been studied sufficiently. There are two contradictory viewpoints. In the opinion of some research workers [1, 3, 4] ferric salts do not react with dimethylglyoxime. On the other hand [5, 6] it is known that the presence of dimethylglyoxime in solution prevents precipitation of ferric hydroxide even at high pH values. Under these conditions an orange-red, transparent solution is formed which is stable on standing. These authors assume that iron is complexed by dimethylglyoxime. Gurvich has established by means of spectrophotometric methods [6] that in a weakly alkaline medium, the ratio of iron to dimethylglyoxime is 1:1 in the compound formed.

We have shown previously [7] that ferric iron prevents complete precipitation of palladium by dimethylglyoxime, and sometimes even completely prevents precipitation of palladium dimethylglyoximate.

In trying to find out the reason for the effect of iron on the reaction between palladium and dimethylglyoxime, we checked on the possibility of a reaction between iron and dimethylglyoxime in an acid medium. Experiment showed that iron also reacts with dimethylglyoxime in an acid medium, when excess of the reagent is present. Nevertheless, the rate of interaction at pH about 3 is very low because of the low degree of dissociation of dimethylglyoxime. In the pH range 2.5-3 equilibrium is attained after about 24 hours, for a dimethylglyoxime concentration of the order of 10^{-3}g.-atom/liter; and iron concentration of the order of 10^{-4}g.-atom/liter; accordingly, we chose this pH range for our studies.

It was found that when a solution of potassium thiocyanate was added to a solution (pH about 3) containing a ferric salt and excess dimethylglyoxime, 24 hours after preparation of the solution the characteristic bright-red color of ferric iron is not obtained. On adding ammonia to this same solution (24 hours after preparing it) first of all there was formed an unstable bright-rose color, changing to orange, which a number of other workers have observed [5, 6] in the case of solutions of dimethylglyoxime and ferric salts in an alkaline medium.

We used a spectrophotometric method for studying the composition of the compound of ferric iron with dimethylglyoxime. Measurements were carried out in the ultraviolet on the SF-4 spectrophotometer. The hydrogen ion concentration in the acid region was determined potentiometrically by means of a glass electrode, while in

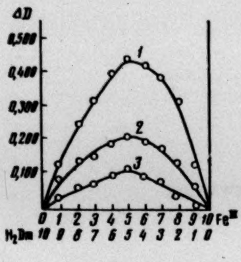

Fig. 1. Determination of composition by the isomolar-series method. C = 4.7 · 10^{-3} g.-atom/liter. 1) 280 mμ; 2) 290 mμ; 3) 300 mμ.

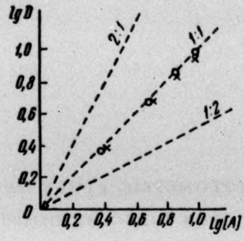

Fig. 2. Determination of the composition of the complex in the acid region. ○) Log [A] = log [H_2Dm]; x) log [A] = log [Fe(III)]; λ = 290mμ.

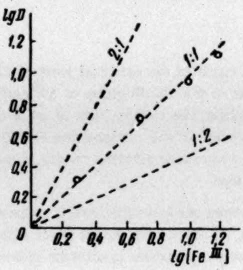

Fig. 3. Composition of the complex in the alkaline region by the method of limiting logarithms.

the alkaline region it was determined titrimetrically.[*]

The composition of the complex was determined by the isomolar-series method, and by the method of "limiting logarithms."

Two isomolar series of solutions of iron and dimethylglyoxime were prepared with total concentrations of 1 · 10^{-3} g.-atom/liter and 4.17 · 10^{-3}g.-atom//liter. The dimethylglyoxime solutions contained 4.8 parts by volume of alcohol. The amount of alcohol and the pH were kept constant in all solutions of both series. In Fig. 1 are given the results of experiments carried out at three wavelengths for the series with a concentration of 4.17 · 10^{-3}g.-atom/liter. The curves which deviate from additivity have maxima at a ratio of the components of 1:1. The same composition was found for the complex by the method of "limiting logarithms," both in series of experiments with excess dimethylglyoxime, and in series of experiments with excess ferric salt. The results obtained are shown in Fig. 2.

The absence of a sharp maximum (Fig. 1) in the given case cannot be regarded as evidence of the low stability of the complex formed in this region. On the contrary, the fact that a complex is formed with dimethylglyoxime, which dissociates only to a very small extent in this region, ($K = 8 \cdot 10^{-12}$) testifies to the high stability of the compound formed.

In addition, we also checked on the composition of the complex in the alkaline region by the method of "limiting logarithms." The composition of the complex was again found to be the same, i.e., Fe : H_2Dm = 1 : 1 (Fig. 3). A series of experiments with a constant concentration of ferric iron and increasing concentrations of dimethylglyoxime gave solutions with constant optical density starting at a ratio of Fe : H_2Dm = 1 : 1. Thus, the results obtained in alkaline media are in full agreement with those of Gurvich [6].

At pH 3, $Fe(OH)^{2+}$ predominates in solution, accordingly, on the basis of the results obtained, it can be postulated that formation of the complex in this region proceeds according to the following over-all equation $Fe(OH)^{2+} + H_2Dm \rightleftharpoons FeOH(HDm)^+ + H^+$.

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[*] A solution of ferric perchlorate was used; this was prepared by repeated evaporation of a ferric chloride solution with perchloric acid until a negative reaction for Cl^- ions was obtained. The dimethylglyoxime solutions were prepared by diluting alcoholic solutions, which were prepared in turn by dissolving an exact amount of the recrystallized reagent in alcohol.

In the complex cation $FeOH(HDm)^+$, iron is apparently connected with the dimethylglyoxime both by valence and coordination bonds. When excess OH^- ions are present, formation of a complex with a different composition, namely FeOHDm, is probable. It is possible that in this compound the bond is only a valence bond. The change over from one form to another proceeds via an unstable, intermediate compound with a bright-rose color.

We tried to evaluate the instability constant of the complex. By analogy with Tolmachev [8], we considered the following equilibria:

$$H_2Dm \rightleftarrows HDm^- + H^+ \quad K_1 = 8 \cdot 10^{-12}$$

$$\frac{HDm^- + Fe(OH)^{2+} \rightleftarrows FeOH(HDm)^+}{H_2Dm + Fe(OH)^{2+} \rightleftarrows FeOH(HDm)^+ + H^+}$$

The constant of the over-all equilibirium $K = [H^+] \cdot [FeOH(HDm)^+] / [H_2Dm] \cdot [Fe(OH)^{2+}]$.

We did not take into account the hydrolysis constant of the iron salts, since it is the group $Fe(OH)^{2+}$ that participates in complex formation.

The instability constant $K_{FeOH(HDm)^+}$ is related to the constants K and K_1 by the following expression: $K_{FeOH(HDm)^+} = K_1/K$.

On the basis of measurements of the optical density at 280 mμ, in preliminary experiments, we determined the molar extinction coefficient of the complex in solutions containing a hundredfold excess of dimethylglyoxime in order to guarantee complexing of the iron

$$\epsilon_{mean} = 1339 \pm 54.$$

Further, on the basis of the values found for the concentration of iron and the complex, we calculated the mean value $K = 2.61 \pm 0.47$, and from this an approximate value for the instability constant of the complex $K_{FeOH(HDm)^+} = 3.06 \cdot 10^{-12}$.

Taking into account the dissociation constant of dimethylglyoxime K_1 and the instability constant of the complex, it is possible, by means of the following equation, to calculate the ratio of the concentration of the complexed and uncomplexed iron:

$$\frac{[FeOH(HDm)^+]}{[Fe(OH)^{2+}]} = \frac{K_1 \cdot [H_2Dm]}{K_{FeOH(HDm)^+} \cdot [H^+]}.$$

This proved to be equal to 4 : 1.

This enabled us to get a more accurate value for the concentration of the complex in each case, and to calculate more accurate values for the molar extinction coefficient for the complex, and then from ϵ_{mean} to find new values of K.

The Table contains values calculated for a pH of 2.59.

$C_{Fe(III)}$ g-at/l original	$[Fe(III)]$ g-at/l free (calculated)	$[FeOH(HDm)^+]$	$D_{complex}$	ϵ_{280}	K for ϵ_{280} 1018 ± ±48
$4 \cdot 10^{-5}$	$8 \cdot 10^{-6}$	$3{,}2 \cdot 10^{-5}$	0,035	1094	3,98
$1 \cdot 10^{-4}$	$2 \cdot 10^{-5}$	$8{,}0 \cdot 10^{-5}$	0,085	1062	3,20
$2 \cdot 10^{-4}$	$4 \cdot 10^{-5}$	$1{,}6 \cdot 10^{-4}$	0,160	1000	2,44
$3 \cdot 10^{-4}$	$6 \cdot 10^{-5}$	$2{,}4 \cdot 10^{-4}$	0,235	979	2,28
$4 \cdot 10^{-4}$	$8 \cdot 10^{-5}$	$3{,}2 \cdot 10^{-4}$	0,306	956	2,11

$$\epsilon^{280}_{mean} = 1018 \pm 48; \quad K_{mean} = 2.80 \pm 0.63$$

From which the value of $K_{FeOH(HDm)^+} = 2.86 \cdot 10^{-12}$.

SUMMARY

It has been shown that ferric iron reacts with dimethylglyoxime to form a complex ion in both acid media (pH about 3) and in alkaline media.

The composition of this complex ion has been shown to correspond to Fe : H_2Dm = 1 : 1 by spectrophotometric methods.

The instability constant of the complex ion $FeOH(HDm)^+$ has been calculated and shown to be $K_{FeOH(HDm)^+} = 2.86 \cdot 10^{-12}$

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A SPECTROGRAPHIC METHOD FOR THE DETERMINATION OF IMPURITIES IN IRIDIUM AND RHODIUM

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Current methods for analyzing rhodium and iridium [1-3] only provide for the determination of a limited number of impurities. This is determined primarily by the complexity of preparing standards, since it is difficult, and sometimes it is also impossible, to introduce all the impurities which accompany rhodium and iridium in ores, or the metals which contaminate iridium and rhodium during the refining process. Our problem was to develop a technique for determining platinum, palladium, gold, ruthenium, iridium, silicon, iron, copper, aluminum, lead, barium, and nickel in rhodium; and platinum, palladium, gold, ruthenium, rhodium, silicon, iron, copper, aluminum, lead, barium, and nickel in iridium.

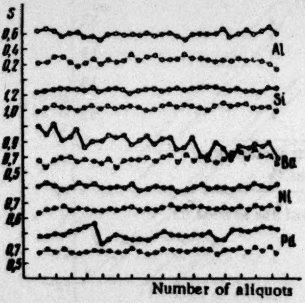

Fig. 1. Distribution of impurities in powdered samples of iridium with diffusion annealing, and without annealing. Each point is the result of one measurement. O–O–O without annealing; O–O with annealing.

Experiment has shown that it is impossible to prepare a fusion standard base on all these impurities. After careful checking we have found that the method described in [3] is the most rational method for use under the conditions we employed. However, the recommended method for preparing standards from solutions is complicated and can only be used as a control method. It has been shown earlier in the case of the spectrographic analysis of silver [4] that the methods of powder metallurgy have possibilities for preparing synthetic standards of noble metals. The opinion has been expressed, [3], however, that it is almost impossible to prepare sufficiently homogeneous samples by mixing the appropriate powders. Accordingly, we decided to compare the methods indicated above for the preparation of standard samples, and to check on the reliability of the latter.

Preparation of Standards. Standard solutions were used as a basis for preparing the standards (Table 1). Aluminum, iron, and lead were dissolved in hydrochloric acid; nickel and copper in nitric acid; platinum, palladium, and gold in aqua regia. The standard solution of a barium salt was prepared by dissolving crystalline barium chloride in water. Silicon was brought into solution by fusion with sodium carbonate and subsequent leaching with water [5]. It is very difficult to dissolve iridium, rhodium, and ruthenium, since they are almost insoluble in acids. The method of dissolving in a reagent tube [3] leads to strong contamination of the solutions by silicon. Yufa and Chentsova have developed the following method for dissolving the noble metals [6]; two sheets of the metal to be dissolved are placed in a 20 % solution of hydrochloric acid; by using an alternating current with a density of 0.5-5 amp/cm^2 the metal dissolves. Standard solutions of rhodium and ruthenium

TABLE 1

Stnd. No.	Concentration, %												Total impurities
	Pt	Pd	Ru	Au	Ba	Si	Rh	Fe	Ni	Cu	Al	Pb	
1	0,005	0,005	0,005	0,005	0,005	0,005	0,1	0,1	0,1	0,1	0,1	0,1	0,630
2	0,01	0,01	0,01	0,01	0,01	0,01	0,04	0,04	0,04	0,04	0,04	0,04	0,084
3	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,024
4	0,04	0,04	0,04	0,04	0,04	0,04	0,01	0,01	0,01	0,01	0,01	0,01	0,084
5	0,1	0,1	0,1	0,1	0,1	0,1	0,005	0,005	0,005	0,005	0,005	0,005	0,630

TABLE 2

Line of the impurity element	Line of the reference element	Transmissivity degree during photometric determination of impurities, %
Rh 3396,85	Ir 3310,52	10
Pd 3421,24	Ir 3310,52	10
Pd 3433,45	Ir 3310,52	10
Pt 2997,97	Ir 2996,08	40
Pt 2702,39	Ir 2656,8	100
Fe 2598,34	Ir 2592,06	100
Fe 4383,54	Background	40
Fe 4325,76	»	40
Au 3122,78	Ir 3310,52	100
Ni 3414,8	Ir 3310,52	40
Si 2881,58	Ir 2996,08	40
Si 2516,12	Ir 2656,8	100
Cu 3273,96	Ir 3310,52	Photometric measurements based on line width [15]
Cu 3247,54	Ir 3310,52	10
Ba 4554,04	Background	10
Pb 4057,82	»	40
Pb 2802,0	Ir 2656,8	100
Ru 3428,31	Ir 3310,52	40
Al 3082,15	Ir 2996,08	10

TABLE 3

Line of the impurity element	Line of the reference element	Transmissivity degree during photometric determination of impurities, %
Pt 3064,71	Rh 3005,82	40 superimposed on the nickel line Ni 3064.62
Pt 2997,96	Rh 3005,82	100
Au 3122,78	Rh 3005,82	100
Pd 3258,78	Rh 3237,66	100
Ir 3133,32	Rh 3005,82	100
Ru 2874,98	Rh 3005,82	100
Fe 2966,90	Rh 3005,82	40
Ni 3037,93	Rh 3005,82	40
Al 3082,15	Rh 3005,82	10
Al 3092,71	Rh 3005,82	10
Cu 3273,96	Rh 3237,66	10
Si 2881,58	Rh 3005,82	100
Si 2528,5	Rh 2629,9	100
Pb 4057,82	Background	40
Pb 3689,47	the same	40
Ba 4554,04	»	10 superimposed on the ruthenium line Ru 4554.50
Pb 2802,00	Rh 3005,90	100
Pb 2833,07	Rh 3005,90	100

were prepared in this way. Spongy metal was dissolved by pressing the latter into sheets which were then subjected to hydrolysis. Iridium dissolves poorly when the electrolytic method is used. The iridium solution was accordingly prepared by dissolving ammonium chloroiridate, the latter is readily soluble in aqua regia; it was then converted into a hydrochloric acid solution.

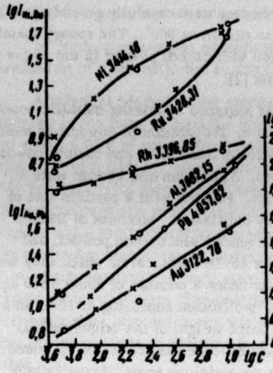

Fig. 2

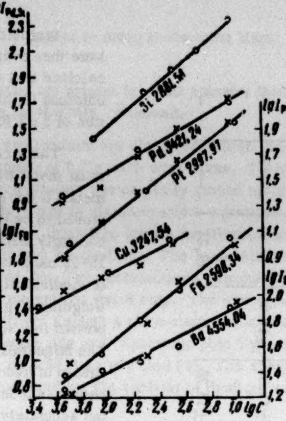

Fig. 3.

Figs. 2 and 3. Comparison of series of standards prepared from solutions and from metallic powders. Each point is the mean of eight measurements. O) Standards made from powders; ×) standards made from solutions.

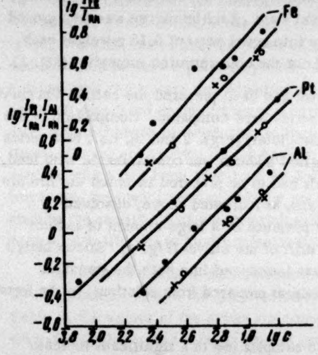

Fig. 4. Calibration curves for iron, platinum, and aluminum in rhodium in the cases where the standards contained about 1% of sodium. ●) Standards from solutions containing about 1% of sodium (about 2% of sodium carbonate); ×) standards prepared from solutions free from sodium; O) standards prepared from powders.

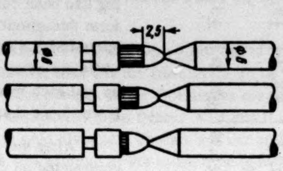

Fig. 5. The shape of the electrodes at different stages in burning.

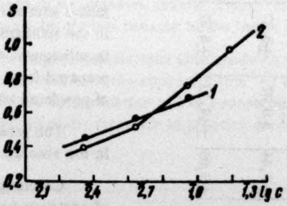

Fig. 6. Effect of third elements during determination of iridium in rhodium, in the case where the internal electrolysis method was used. 1) Iridium in rhodium; 2) iridium containing rhodium as impurities.

TABLE 4

Test element	Ni	Pd	Si	Cu	Fe	Ba	Pt	Al	Pb	Ru	Au	Rh	Ir
Mean relative error for a single determination of the concentration of impurities in iridium	±6,44	±6,67	±6,67	±7,13	±7,82	±8,51	±9,66	±9,89	±11,27	±11,96	—	10,12	—
Ditto for rhodium	±8,05	±16,10	±6,67	±9,89	±5,98	±21,23	±5,70	±6,90	±18,26	—	13,34	—	—

Standards were prepared by mixing these solutions. The solutions were then evaporated to dryness; the residues were carefully ground up and calcined in a tubular oven in a hydrogen stream at 900°. The spongy metal obtained in this way was carefully mixed with carbon powder in the proportion of 2 : 1 for 12 hours in a glass mixer [7].

The second series of standards was prepared by mixing metallic powders, using metal from the same batch as a base. Preparation of powders of most metals is not complicated [8]. Preparation of aluminum and barium powders proved to be comparatively complicated. Aluminum and barium were accordingly used in the form of their oxides. Powders with a particle size of 15-20 mesh were prepared for mixing by elutriation. Mixtures of iridium or rhodium with the impurities to be introduced plus carbon powder, and weighing 20 g were mixed in a mixer for 15-18 hours, after which they were pressed in a steel die 20 mm in diameter under a pressure of about 1600 kg/cm^2. The briquettes obtained were subjected to diffusion annealing at 1000° in a stream of hydrogen for 5-6 hours. The large weight of the briquettes was chosen in order to ensure that the impurities to be used could be measured out accurately enough, and to decrease the weighing error. Actually only 0.15 g of such a mixture is required for an analysis, accordingly the twenty briquettes were ground up in a mortar after they had been annealed. Aliquots of 0.15 g were then taken from the mixtures for analysis.

The standards prepared from powders were checked to ensure that mixing had been complete and that the concentrations of the impurities was uniform throughout the volume of the sample on annealing. For this purpose two briquettes 8 g each were prepared, one of which was subjected to annealing, while the other was left in its original state. Each briquettes was then ground up and each mixture was divided up into equal parts of 0.15 g weight each. It was found that annealing leveled out the concentration somewhat (Fig. 1).

After the two series of standards had been prepared the calibration curves constructed on the basis of the two series were compared. Comparison of the curves showed that they coincide completely (Figs. 2 and 3), i.e., both series of standards are identical. The original iridium was contaminated with lead, accordingly a second set of standards had to be prepared in which the iridium was free from lead. Silicon was again, as indicated above, dissolved by fusion with sodium carbonate. The presence of a large amount of sodium in the standards leads to a parallel shift of the curves (Fig. 4). Accordingly, in subsequent experiments silicon was introduced into both the standards prepared from powders and into standards prepared from solutions, in the form of powdered silicon metal.

The presence of sodium in the samples led to a significant increase in the absolute sensitivity of the determination of the elements (Fig. 4).

Calculation of contamination of the base was checked by the method of additions both graphically [9] and analytically [10]. In those cases where the curve I = f(C) is curvilinear, it is possible to use Akimov's recommendations [11]. All three methods of calculating the contamination of the base gave almost identical results.

Third-element effects can be disregarded as long as the total of all the elements or of one element does not exceed about one percent. Above this limit the intensity of the base decreases; accordingly, standards were prepared so that the total amount of all the impurities introduced into the base did not exceed 0.6% (see Table 1). One can only speak of third-element effects in connection with the standards, since many elements are present in them at the same time. But this fact, as indicated above, was taken into account.

In production samples of iridium and rhodium the impurities are present in small amounts (hundredths and thousandths of a percent), but in this case third-element effects are scarcely observed.

Analytical Method. The methods for analyzing iridium and rhodium are almost identical. Iridium was analyzed in the form of metallic powder, from which three aliquots of 0.1 g each were taken. To each aliquot was added 0.05 g of spectrographically pure graphite powder, the mixture was carefully ground up in a mortar reinforced with iridium, after which it was pressed in a steel die 4 mm in diameter under a pressure of 4000-5000 kg/cm^2. The spectrograph used was a KS-55 apparatus with a three-lens system for illuminating the slit. The spectrograph slit width was 0.017 mm for iridium, and 0.025 mm for rhodium. The lower electrode was a graphite rod 6 mm in diameter sharpened to a truncated cone (Fig. 5). The interelectrode distance was 2.5 mm. The excitation source was an activated ac arc (DG generator), the current was 8 amp. The exposure time was 60 se. Each standard and each sample was photographed three times through a three-stage attenuator. The photographic plates used were "Spectrographic Type I" for the long-wave side and "Spectrographic Type II" for the short-wave side; the developer was metol–hydroquinone [12], an acid fixer was used [9]. The analytical pair of lines for the analysis of iridium are given in Table 2, while those used for the analysis of rhodium are given in Table 3.

During analysis of iridium the sensitivity of the determination of rhodium was approximately 0.01%, while for all the remaining elements it was about a thousandth of a percent. For the analysis of rhodium at a comparatively good sensitivity for the determination of all the elements (thousandths of a percent) iridium, and ruthenium could only be determined starting at a level of 0.1%. In order to increase the sensitivity for the determination of iridium we used the so-called method of internal electrolysis [13, 14] which has been used for the determination of lead (0.0001) in iron.

In our experiment we used dilute hydrochloric acid solutions of rhodium with additions of iridium. Aluminum was selected as the anode, while the cathode was gold. In order to take out the iridium 10 ml of test solution was taken, in which short-circuited plates of aluminum and gold were placed. After 90 minutes the aluminum plate and the solution were replaced by fresh ones. This process was repeated three times. As a result of this procedure a dense gray precipitate was deposited on the gold plate. The gold plate plus deposit was cut up into three parts and each part fused in the crater of a carbon electrode which was exposed at the same time (globule arc). By using this technique we were able to increase the sensitivity for the determination of iridium in rhodium five times. Curves constructed on the basis of standards in which only iridium was present, and on the basis of standards to which had been added all the impurities, almost coincide with each other, i.e., the presence of third impurities does not interfere with the precipitation of iridium (Fig. 6). Thus, the internal electrolysis method enables the sensitivity of the determination of iridium in rhodium to be increased several times. The method of determining iridium in rhodium is not suitable from an economic point of view because of the use of gold electrodes.

In order to evaluate the reproducibility of the method developed, calculations were made on the basis of 40-50 measurements of the mean relative error of a single determination of the concentration. As is evident from Table 4, the values of the errors are completely satisfactory for the determination of low concentrations, and, since the analysis, as a rule, is carried out on two-three parallel aliquots, this error in practice decreases several times.

SUMMARY.

It has been shown that it is possible to prepare standards for the spectrographic analysis of iridium and rhodium from metallic powders. A method is given for the spectrographic analysis of iridium and rhodium for their content of twelve elements present as impurities.

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DETERMINATION OF MICROGRAM AMOUNTS OF BORON IN COMPLEX ALLOYS

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Methods for the determination of small amounts of boron in modern, complex alloys do not give reliable results and are difficult to carry out. The method adopted in analytical practice involves multiple and long distillations of boron in the form of methyl borate.

The aim of the work described here was to look for a rapid, simple, and accurate method for the determination of microgram amounts of boron in complex alloys based on nickel, iron, cobalt, and titanium and containing tungsten, niobium, molybdenum, chromium, silicon, and other elements using aliquots of 0.01-0.05 g.

Small aliquots and small volumes of solution cut down the time for determining boron in alloys sharply, simplify separation of accompanying elements, and strongly decrease the boron content in the control experiment.

Among the various reagents used for the photometric determination of boron [1-23], alizarin, quinalizarin, and carminic acid are the ones which have been used most widely.

During a comparative study of such reagents as curcumin, quinalizarin, chromotrope-2B, carminic acid, and the recently suggested reagent arsenazo-2, we established that the last three reagents give the best results for the determination of gamma amounts of boron.

Carminic acid was first suggested for the determination of boron by Zorkin [1]. It has been used for the quantitative determination of boron in borate ores by Kazarinova-Oknina [2]. It has also been recommended that boron can be determined by means of a 0.005% solution of carminic acid in concentrated sulfuric acid. This has made it possible to determine microgram amounts of boron in water, salts, and solids with satisfactory accuracy [3].

In order to establish the effect of time on the development of the maximum color of the complex of boron with carminic acid, experiments were carried out on the spectrophotometric determination of boron in which the optical density (cuvette 10 mm; relative to concentrated H_2SO_4; $\lambda = 575\ m\mu$) was measured at intervals of 15 minutes. After standing for 4 hours the color of solutions of the complex was stable; the values were unchanged after 24 hours. Experiments showed that by means of carminic acid it is possible to determine 1 μg of boron in the presence of not more than 10 μg Ti^{IV}, 50 μg Mo^{VI}, 50 μg Fe^{III}, 75 μg W^{VI}, and 200 μg Ni^{II}.

We have tested a spectrophotometric determination of microgram amounts of boron with the following reagents: chromotrope-2B suggested by Komarovskii and Poluéktov [4-5], and the new reagent arsenazo-2 synthesized by Kuznetsov for color reactions with uranium and thorium [6].

Development of the color of the compound formed between boron and a 0.01% solution of chromotrope-2B in concentrated sulfuric acid is complete in 45 minutes. The color of a solution of the complex is stable for 24 hours. The color changes from violet to blue in the presence of boron. Determination of tenths of a microgram of boron is most conveniently carried out in a volume of 3 ml with 0.5 ml reagent. The sensitivity of the detection

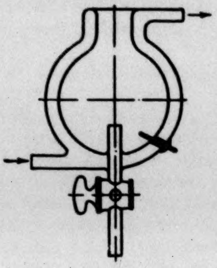

Fig. 1. Funnel-electrolyzer.

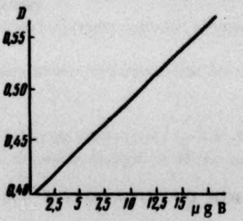

Fig. 2. Calibration curve for the determination of boron in titanium alloys by means of arsenazo-2.

of boron with chromotrope-2B amounts to 0.07 μg B/ml. The limiting dilution is 1 : 20,000,000. It is possible to determine 1 μg of boron by means of a 0.01% solution of chromotrope-2B in the presence of not more than 5 μg Ti^{IV}, 5 μg W^{VI}, 55 μg Mo^{VI}, 75 μg Ni^{II}, and 100 μg Fe^{III}. Full development of the color of the complex formed between boron and a 0.005% solution (in concentrated sulfuric acid) of arsenazo-2 occurs in 35 minutes. In the presence of boron the color of the reagent changes from violet to blue, which does not change in the course of 24 hours. Tenths of a microgram of boron can be conveniently determined in a volume of 3-4 ml with 0.5 ml of reagent (0.005% solution). The sensitivity of the detection of boron with arsenazo is 0.1 μg B/ml. The limiting dilution is 1 : 10,000,000.

One microgram of B can be detected with arsenazo-2 in the presence of 75 μg Ti^{IV}, 100 μg W^{VI}, 100 μg Mo^{VI}, 125 μg Ni^{II}, and 125 μg Fe^{III}. Thus boron can be determined by means of arsenazo-2 at a more favorable ratio of boron to the other elements.

Solutions of the complexes of boron with chromotrope-2B and arsenazo-2 conform to Beer's law. These two reagents permit determination of microgram amounts of boron with satisfactory accuracy. The methods which we have developed permit the determination of 0.01% and higher of boron in various modern complex alloys.

It is known that for the determination of small amounts of boron, it is usually recommended that the amount of alloy taken for analysis should be increased to 2 g [13, 15]. When, however, such large aliquots are used, difficulties arise in connection with complete dissolution of complex alloys in sulfuric acid, and also in connection with the time such dissolution takes. Moreover, when such large aliquots are used, it is difficult to oxidize large amounts of carbides completely. A large excess of oxidizing agent has to be taken, and subsequent decomposition of the latter means a very prolonged boiling of the solution.

The high sensitivity of the reagents chosen permits boron to be determined on small aliquots (0.01-0.05 g). Dissolution of this size of sample of a complex alloy proceeds rapidly (about 15 minutes). Large amounts of oxidizing agent are not required for oxidizing the solution.

The aliquot of alloy (0.05 g) was dissolved in 1 ml H_2SO_4 (1 : 2) in a 20 ml quartz vessel connected via a ground joint to an eight bulb reflux condenser cooled with tap water; it was dissolved on gentle warming on a hot plate (on asbestos). This amount of acid proved to be the optimum for dissolving 0.05 g of alloy. Increasing the amount of acid used to dissolve the alloy is undesirable, since increasing the volume of the solution complicates subsequent analytical operations, particularly the electrolysis on a mercury cathode. Of special importance is the choice of oxidizing agent and the amount of it used, after dissolving the alloys in sulfuric acid. It was established that 3% hydrogen peroxide does not oxidize the carbides completely; even after boiling for a long time a black residue was left on the bottom of the flask. When 3 ml of 30% hydrogen peroxide was used the carbides were completely oxidized in 45 minutes boiling, but the color from the titanium compound with hydrogen peroxide did not disappear. Ammonium persulfate proved to be the most efficient oxidizing agent for the determination of boron in alloys containing titanium. Oxidation of a test solution of the alloy in the presence of 0.2 ml of a 1% solution of silver nitrate made it possible to cut down the amount of oxidizing agent to 0.5 ml of 25% ammonium persulfate solution, with subsequent boiling of the solution for 12 minutes. The carbides were completely oxidized.

TABLE 1

Comparative Results for the Determination of Boron in Alloys by Means of Carminic Acid (Aliquot 0.05 g, 575 mμ)

By the distillation method [13,15,19,20,23] in the form of $B(OCH_3)_4$, %	By suggested method, %		Difference, %
0,009	0,010;	0,010	+0,001
0,010	0,010;	0,010	—
0,030	0,030;	0,032	+0,001
0,035	0,035;	0,033	—0,001
0,047	0,046;	0,046	—0,001
0,050	0,055;	0,055	+0,055

TABLE 2

Spectrophotometric Determination of Small Amounts of Boron in Complex Alloys by Means of Carminic Acid (Aliquot 0.05 g, 575 mμ)

Alloy	Boron content, %	Boron found, %	Difference, %
Chromenickel alloy based on Ni	0,006	0,066	+0,0002
The same	0,015	0,015	—
» »	0,025	0,0245	—0,0005
» »	0,045	0,045	—
Alloy based on Co	0,014	0,015	+0,001
The same	0,020	0,020	—0,0001
» »	0,028	0,029	0,001
» »	0,060	0,060	—
Alloy based on Fe*	0,022 **	0,020	—0,002
The same	0,031 **	0,030	0,001
» »	0,040 **	0,040	—
» »	0,060 **	0,061	0,001

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* 0.025 g aliquot.

** Boron was introduced into a solution of the alloy in the form of H_3BO_3 (standard solution).

TABLE 3

Spectrophotometric Determination of Small Amounts of Boron in Titanium Alloys by the Method of Additions (Aliquot 0.01 g)

Contained in the alloy, %	Found %	Difference, %	Reagent
0,005	0,0048	—0,0002	Arsenazo-2 (640 mμ)
0,010	0,0096	—0,0004	
0,015	0,0152	+0,0002	
0,015	0,0153	+0,0003	Carminic acid (575 mμ)
0,020	0,021	+0,001	
0,025	0,026	+0,001	
0,005	0,0056	+0,0006	Chromotrope-2B (620 mμ)
0,0075	0,0075	—	
0,0125	0,0130	+0,0005	

Special experiments showed that no boron is lost during dissolution of the alloy.

A mercury cathode was used for removing accompanying elements from boron after the aliquot of alloy had been dissolved. A mercury cathode has been used for the volumetric determination of boron by Chizhevskii [7] and Kar [8].

We should like to put forward a model of a funnel-electrolyzer (Fig. 1) for separating boron from interfering elements; it is made from glass and has double walls between which water circulates continuously. The capacity of the funnel is 35 ml. We have also tested a model of a funnel-electrolyzer with a capacity of 5 ml, for carrying out experiments in a small volume. Cooling of the electrolyzer with tap water during electrolysis enables the temperature of the electrolyzer to be kept below 25°.

Boron was separated from titanium and zirconium (after electrolysis with a mercury cathode) by means of alkali.*

After removal of titanium and zirconium with alkali, the solution containing boron was evaporated with concentrated H_2SO_4. According to published data [14], acid evaporation without loss of boron is possible when alkali metal salts are present. Our experiments confirmed this.

Comparative results of the determination of boron (Table 1) showed that the method we have developed has good accuracy and reproducibility.

By using small aliquots and small volumes of solution, and by using alkali with a high degree of purity, the amount of boron in the control experiments is very insignificant and does not reflect on the determination of boron.

On the basis of the results obtained, experiments were carried out on the spectrophotometric determination of boron in alloys based on nickel, cobalt, and iron.

The most complicated problem in the determination of boron in alloys based on titanium is the separation of boron from titanium.

We used an alkali separation. Many experiments with various microgram amounts of boron showed that during the alkali separation, boron is not absorbed by the titanium precipitate (0.01 g aliquot), and does volatilize during the subsequent acid evaporation.

A check on the completeness of precipitation of titanium (0.01 g) with alkali was carried out in all the experiments. After filtering off the precipitate, titanium could not be detected in the sulfuric acid solution by means of hydrogen peroxide.

After removing the titanium with alkali and evaporating with H_2SO_4, boron can be finally determined by means of carminic acid, chromotrope-2B, and arsenazo-2. For low boron contents in titanium alloys, it is convenient to determine boron by the method of additions (Table 3).

Analytical Procedure for Chromonickel, Cobalt, and Iron** Alloys. 0.05 g of finely ground ribbon is placed in the 20 ml quartz vessel, the diameter of the bottom of which is 20 mm; this vessel is connected via a ground joint to an eight bulb reflux condenser; the aliquot is dissolved*** in 1 ml of H_2SO_4 (1 : 2) on gentle warming on an asbestos sheet placed on a hot plate. Dissolution is complete in 15-20 minutes, depending on the degree to which the sample has been ground. In order to avoid heating the neck of the flask, it is covered with asbestos. When the sample has dissolved the flask is cooled and disconnected from the condenser. 0.5 ml of a freshly prepared 25% solution of ammonium persulfate is added and 0.2 ml of a 1% solution of silver nitrate. The flask is connected to the condenser and the solution heated to the boil and boiled for 15 minutes until excess oxidizing agent has been completely destroyed (cessation of liberation of bubbles).

Heating is stopped, and without disconnecting the flask, three lots, 3 ml each, of cold distilled water are poured through the top of the condenser to wash the walls down. The flask is then disconnected and the solution filtered free from the precipitate of tungstic and niobic acids, the filter is washed twice with water. The filtrate is diluted to 15 ml with water and is transferred to the electrolyzer containing a mercury cathode. The funnel-electrolyzer has double glass walls through which circulates tap water for cooling the solution in order to avoid volatilization of the boron. The temperature of the solution should not exceed 20°. After 15-20 minutes the decolorized solution is tested for absence of Ni, Co, Fe, and Cr (depending on the alloy base) by means of spot reactions. Next, without switching off the current, the solution from the electrolyzer is poured through the funnel into a quartz beaker. The mercury surface is washed four times with 2.5 ml portions of distilled water added by means of a pipet. 2.5 ml of a 40% solution of NaOH is added by means of a pipet and the solution heated on the water bath until the precipitate has coagulated. The precipitate which contains titanium and zirconium is filtered off, washed three times with 1 ml lots of 1% NaOH and then discarded. To the filtrate in the quartz beaker is added concentrated H_2SO_4 dropwise, until the solution gives an acid reaction to congo red paper. Another 10 ml of concentrated H_2SO_4 is added by means of a pipet, followed by 2-3 drops of HNO_3 (1.40), and the solution evaporated twice until the appearance of thick white fumes, which are allowed to come off for 5 minutes. After the flask has been cooled, 10 ml of a 0.005% solution of carminic acid in concentrated H_2SO_4 is added, and the solution allowed to stand for 4 hours for the color to develop completely (it can be left overnight).

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* Kal'baum and Merck alkali was used.

** 0.025 g aliquots are used for alloys based on iron.

*** All the reagents must be measured out with a pipet.

The optical density of the solution is measured at 575 mμ in a 10 mm quartz curvette on a SF-4 apparatus. Concentrated H_2SO_4 is poured into the parallel cuvette. A control solution which is taken through all the stages of the analysis is prepared for each series of determinations. Chromotrope-2B and arsenazo-2 can be used instead of carminic acid (see analytical procedure for titanium alloys).

Determination can also be carried out visually by the standard-series method.

It is best to construct a calibration curve for each alloy, using alloys similar in composition but free from boron. The boron is introduced as a standard solution of H_3BO_3.

Analytical Procedure for Titanium Alloys. 0.01 g of titanium alloy is dissolved in the quartz vessel connected to an eight bulb condenser via a ground joint, using 1 ml of H_2SO_4 1 : 3. When the aliquot has dissolved, 0.15 ml of a 15% solution of ammonium persulfate is added by means of a pipet in order to oxidize the solution; after 20 minutes moderate boiling the solution is cooled. The solution should be colorless. 1 ml of water is added through the top of the condenser. The contents of the quartz flask are transferred to a 25 ml quartz beaker and congo red indicator paper immersed in it. 2.5 ml of 40% NaOH is added. The solution is heated on a water bath until the precipitate has coagulated, the latter is filtered through a small funnel fitted with white band filter paper and a small amount of macerated paper. The first portion of filtrate is returned from a second passage through the filter. The filter plus precipitate are washed three times with 1 ml lots of 1% NaOH (when the test alloy contains chromium and nickel, the solution is electrolyzed on a mercury cathode). To the filtrate is added 7 ml of concentrated H_2SO_4, 5 drops of concentrated HNO_3* and the solution evaporated until white fumes of sulfuric acid come off. These are allowed to come off for 5 minutes.

On cooling, 2 ml of a 0.025% solution of carminic acid, or 3 ml of a 0.01% solution of chromotrope-2B, or 3 ml of a 0.005% solution of arsenazo-2 is added, and the optical density measured on a SF-4 spectrophotometer. For the determination of 0.005-0.03% of boron in titanium alloys it is best to use the method of additions.

SUMMARY

A simple and accurate method is suggested for the determination of microgram amounts of boron in small aliquots of alloys based on nickel, cobalt, iron, and titanium. The method does not require preliminary distillation of boron as methyl borate. Separation of boron from accompanying element is effected on a mercury cathode.

Optimum conditions have been established for the spectrophotometric determination of microgram amounts of boron in various alloys, using carminic acid, chromotrope-2B, and arsenazo-2 as reagents.

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* Original Russian pagination. See C. B. translation.

CONDUCTOMETRIC MICRODETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS

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So-called manual methods predominate to a significant extent in elemental organic analysis; the results obtained when such methods are used depend to a certain extent on the individual characteristics of the analyst. We have set ourselves the problem of developing a method for an objective instrumental finish for the determination of carbon and hydrogen. A conductometric method was chosen as the means for measuring the amounts of the final combustion products – carbon dioxide and water. Existing variants of the conductometric determination of low contents of carbon[1-7] have proved insufficiently accurate for organic analysis, in which it is required to determine a high carbon content in an aliquot with a relative error of 0.2-1%. The necessary accuracy was achieved after constructing cells for measuring the electrical conductivity which answered the specific requirements of elemental microanalysis. The basis of the conductometric determination of hydrogen is based on the interaction between water and carbon at high temperatures in an inert gas atmosphere, according to the scheme: $C + H_2O = CO + H_2$. This reaction has been used for the direct determination of oxygen [8-11], and for the iodometric determination of hydrogen in organic compounds [12], and also for the determination of small amounts of water in gases [13]. We have used it for the conductometric determination of hydrogen in organic material on one aliquot together with carbon [14].

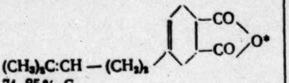
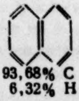
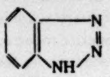
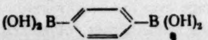
The determination is carried out in two stages. First of all an aliquot of organic material is subjected to pyrolytic combustion in an unfilled tube in a rapid stream of oxygen [15]. The water obtained is frozen out with a mixture of dry ice (solid CO_2) and acetone, while the carbon dioxide is passed into a cell containing dilute alkali in order to determine the conductivity. The frozen water is then evaporated in an argon or nitrogen stream onto a contact layer of platinized carbon black [11], where the oxygen of the water reacts with carbon to form CO. The CO is subsequently heated over cupric oxide [11] to CO_2, and the latter passed into the cell for electrical conductivity measurement. Thus, both carbon and hydrogen are determined on the basis of the change in electrical conductivity of the absorbing solution.

Conductometric determination of carbon and hydrogen has the advantage over the usual gravimetric determination in that the reproducibility of the results is better; this should be related to the higher "objectivity" of the measurements, and the elimination of factors which affect the accuracy of the results, such as changes in atmospheric conditions, electrical charging of the surface of the apparatus being weighed, errors in the weights and riders. In addition, such a measurement technique permits one to study the combustion of aliquots with time, which is of undoubted interest. And, finally, measurements of electrical conductivity can be unconditionally automatized.

Simultaneously with development of an instrumental finish for the analysis, we also wished to carry out combustion of test material without any supervision from the analyst. Determination of carbon and hydrogen consists of three stages: taking samples, combustion of test material, and measurement of the final combustion products. The most difficult are the two last stages. Attempts to automatize elemental microanalysis have been made re-

TABLE 1

Microdetermination of Carbon and Hydrogen

Material	Aliquot, mg	C, %		H, %	
		found	difference	found	difference
CH_3COCH_3	1,470	61,96	—0,07	10,47	+0,05
62,03% C 10,42% H	0,906	61,80	—0,23	10,56	+0,14
$C_2H_5OC_2H_5$	1,853	65,03	+0,17	13,69	+0,18
64,86% C 13,51% H	0,716	64,86	0,00	13,56	+0,05
C_6H_5COOH *	1,229	69,02	+0,16	5,16	+0,18
68,86% C 4,98% H	1,020	68,82	—0,04	5,04	+0,06
	1,052	72,05	+0,20	7,74	+0,04
71,85% C 7,70% H	1,172	71,76	—0,09	7,66	—0,04
	0,988	93,56	—0,08	6,47	+0,15
93,68% C 6,32% H	0,710	93,38	—0,30	6,60	+0,28
	1,006	60,77	+0,27	4,33	+0,10
60,50% C 4,23% H	0,934	60,47	—0,03	4,24	+0,01
$C_6H_2(OH)(NO_2)_3$	2,257	31,50	+0,05	1,35	+0,03
31,45% C 1,32% H	1,652	31,67	+0,22	1,30	—0,02
$CCl_3CH_2CHBrCH_2OC(:O)CCl_3$	2,248	17,90	—0,04	1,19	—0,07
17,94% C 1,26% H	2,974	18,05	+0,11	1,16	—0,10
$CCl_2{=}CClCH_2SO_2C_6H_5$	1,112	37,82	—0,02	2,46	+0,01
37,84% C 2,45% H	1,488	37,98	+0,14	2,63	+0,17
$(CF_3CF_2CF_2CF_2CONH_2)_2$	1,738	24,35	—0,24	0,77	—0,05
24,59% C 0,82% H	1,689	24,44	—0,15	0,77	—0,05
$(CH_3)_3SiCH(CH_3)CN$	1,755	56,59	—0,04	10,08	—0,22
58,63% C 10,30% H	1,487	56,82	+0,19	10,21	—0,09
	1,077	43,34	—0,17	5,02	+0,15
43,51% C 4,87% H	0,911	43,47	—0,04	5,12	+0,25
$(CH_3)_2NC_6H_4HgNHC_6H_4NO$ *	1,980	38,33	+0,23	3,51	+0,11
38,10% C 3,40% H	1,743	38,32	+0,22	3,44	+0,04
$(n\text{-}C_3H_7)_2SnO$ *	1,320	32,80	+0,19	6,44	+0,06
32,61% C 6,38% H	1,374	32,68	+0,07	6,36	—0,02

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* Combustion was carried out by means of an oven moved forward automatically.

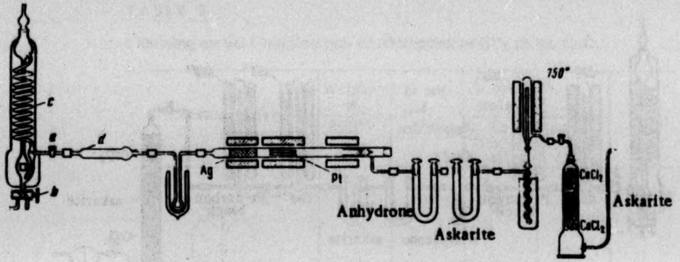


Fig. 1. Setup for the combustion and determination of carbon.

peatedly, but all these attempts have been directed solely at the second stage, namely to combustion of the aliquots. For this purpose various types of heater have been suggested which move forward at a given rate and are stopped or switched off when the pressure inside the tube increases [16-19]. The most expedient method for automation of this stage of the organic analysis is to create optimum conditions for combustion, high temperatures and a large excess of oxygen, when regulation of the combustion process becomes unnecessary. An example of this is the combustion of organic halogen compounds carried out by Wickbold [20] in an oxygen-hydrogen flame, both gases being passed through at high rates directly from cylinders, or combustion of metals by Malissa [7] at 1000° and an oxygen rate measured in hundreds of ml per minute. Nevertheless, we were able to achieve rapid quantitative combustion using significantly lower oxygen rates, and not such high temperatures. By increasing the ratio of the rate of oxygen to sample five times, by cutting down the sample weight to 1 mg, combustion without supervision from the analyst could be carried out in 3-5 minutes.

The method suggested has been used for carbon and hydrogen determination in 65 organic compounds of different composition and properties [30]. Examples are given in Table 1.

Apparatus. The apparatus for C and H determination consists of a combustion setup, a setup for conversion of water, and apparatuses for measuring electrical conductivity.

Combustion Setup (Fig. 1). The usual setup for rapid determination of C and H [15, 21] is used, but instead of absorption apparatus and Mariott flasks, a trap for freezing out the water, and a cell for determining CO_2 from the change in electrical conductivity are connected to the combustion tube.

The trap is a thick-walled quartz capillary U-tube in which the capillary diameter is 1 mm, the length of each arm of the U-part being 70 mm and the length of each lead-out tube being 50 mm.

Setup for Conversion of Water (Fig. 2) consists of a system for purifying the inert gas (argon or nitrogen) from traces of oxygen (see [11]), a trap with the frozen water, a Dewar vessel, a three-way tap, a contact apparatus with platinized carbon black heated to 900°, and the oxidizing apparatus containing cupric oxide, to which the cell is connected directly. When the contact apparatus is being filled with platinized carbon black, it is necessary to put on the bottom of the apparatus sufficient broken quartz so that the layer of platinized carbon-black is heated along its whole length to the requisite temperature.

Test materials are weighed on a Bunge microbalance.

The Apparatus for Measuring the Electrical Conductivity is based on a Wheatstone bridge and consists of a sound generator (ZG-10) as an ac source, a dc bridge (MTV), the three-component resistances of which serve as three arms of the Wheatstone bridge, a capacity box (ME-3) for compensation and self-inductance, an electronic oscillograph (ÉO-7) as a zero instrument, and two working cells for measuring electrical conductivity.

The Cell for Measuring the Electrical Conductivity. As a result of the combustion of 1 mg of an organic compound, 3.5 mg of carbon dioxide is formed which passes into the cell together with the oxygen stream passing through the apparatus at the rate of 30 ml/minute, a large fraction of this CO_2 passes into the cell in the course of 2-3 minutes. It is necessary under these conditions to ensure complete absorption of CO_2 and to level out the concentration of the absorption solution in the shortest possible time. Cells designed previously [3, 6, 22] for the

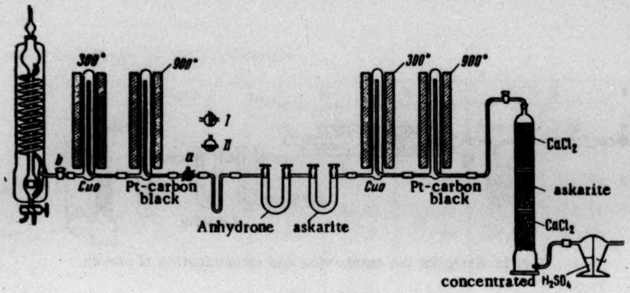

300°
900°
I
II
a
b
CuO
Pt-carbon black
Anhydrone
askarite
300°
900°
CuO
Pt-carbon black
CaCl₂
askarite
CaCl₂
concentrated H₂SO₄

Fig. 2. Setup for converting the water.

determination of small amounts of carbon proved inapplicable for measuring such small amounts of CO_2. Below is given the description of a cell modified by the authors so that it would answer the demands placed on it (Fig. 3). The gas containing the CO_2 formed passes through the side tap a and the capillary spot b into the cell, and

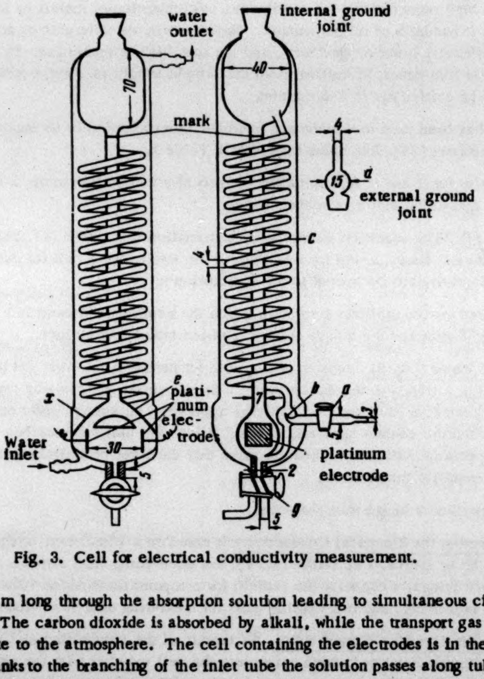
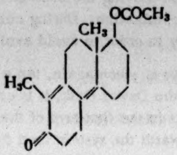

water outlet
internal ground joint
70
40
mark
4
15
d
external ground joint
c
x
e
platinum electrodes
30
Water inlet
f
7
b
a
platinum electrode
2
g
5

Fig. 3. Cell for electrical conductivity measurement.

bubbles along a coil 2 m long through the absorption solution leading to simultaneous circulation of the liquid along the whole cell. The carbon dioxide is absorbed by alkali, while the transport gas passes through a guard tube containing askarite to the atmosphere. The cell containing the electrodes is in the form of a horizontally arranged cylinder. Thanks to the branching of the inlet tube the solution passes along tubes e and f directly onto the electrodes, the dead space between the electrode and the wall of the cell is eliminated, and complete mixing of the solution is speeded up. Two platinum plates 13 x 13 mm serve as the electrodes. The distance between them is 30 mm. The smooth surface and the vertical arrangement of the electrodes permits one to reduce

TABLE 2

Checking on the Completeness of Absorption of CO_2 in the Cell.

Test material	Weight of aliquot, mg	Gas output, ml/min	C found, % (relative)		Total
			In the first cell	In the second cell	
	1,015	30	100,2	0	100,2
	0,987		99.9	0	99,9
	0,994	45	99,4	0,6	100,0
% C =75,00	1,002		96,6	3,0	99,6

to a minimum errors arising from deposition of solid particles of $BaCO_3$ [when a $Ba(OH)_2$ solution is used as absorbent] on the platinum surface. The cell is filled (to the mark) and the solution is replaced through a lower three-way tap g. The capacity of the cell is 55 ml. The cell has a water jacket and is thermostatted at 25 ± 0.1°. Experiments carried out with two cells connected in series showed that at a gas rate of 30 ml/ min CO_2 is completely absorbed. On increasing the rate 1.5 times, i.e., to 45 ml/ min some of the CO_2 was found to have passed into the second cell (Table 2). A cell of the same design is also used for the determination of hydrogen in organic materials [14].

1) Reagents. Cupric oxide in wire form. The carbon black which is granulated contains 50% platinum absorbed by Bondarevskii's method [23]. The residue after evaporation, without additional drying, is calcined while the temperature of the oven is gradually increased.

2) Anhydrone. 3) Askarite. 4) Nitrogen or argon of the highest purity.

5) 0.01 Solutions of NaOH or $Ba(OH)_2$ are prepared by dissolving 2 g NaOH (analytical grade) or 8 g Ba $Ba(OH)_2 \cdot 8H_2O$ (analytical grade), respectively, in 5 liters of boiled water free from CO_2. After standing for 24 hours the clear part of the solution is decanted.

Analytical Procedure. Taking Samples. The analysis is carried out with about 1 mg, i.e., about a fifth of the amount used in microanalysis. In order to avoid errors connected with the weighing of the comparatively large quartz test tubes in which the combustion is carried out, the aliquot is placed in a small platinum boat, which, prior to combustion is placed in an empty quartz test tube which is always kept in the combustion tube. This method of introducing the sample decreases the error of the blank run, since the minimum amount of contaminated laboratory air is allowed into the setup, and the time for sweeping the apparatus with oxygen prior to combustion is cut down.

Analytical Procedure when 0.01 N $Ba(OH)_2$ Solution is Used as the Absorbent. The apparatus is assembled as shown in Figs. 1 and 2. The cell used for measuring the electrical conductivity (Fig. 3) is washed twice with 0.01 N $Ba(OH)_2$ solution. Tap b is used for filling and emptying. The side tap b(Fig. 1) should be closed. The cell is then filled with the same solution to the mark, and by steadily turning tap a oxygen is allowed to start bubbling through coil c. The position of the side tap is regulated so that the level of the solution in the cell rises to a line previously marked out with a dye on the outer surface of the glass jacket surrounding the coil. This line corresponds to a gas throughput of 30 ml/ min.

While the apparatus is being swept out (5 min) with oxygen, an aliquot of about 1 mg is weighed out; with tap a closed (Fig. 1) the quartz test tube is removed from the combustion tube and the boat plus sample placed in it, and the quartz tube then replaced in the combustion tube. Tap a is opened again, and after 2-4 min the resistance reading becomes constant enough (an increase of about 0.2 ohm per minute for a total resistance of 330 ohms). Measurement of the resistance is carried out for an ac frequency of 1,000 cps, and a voltage of 4 volts, for a resistance of the two arms of the bridge of 100 ohms each, and for the maximum increase in the vertical and horizontal inputs of the oscillograph. When the bridge is unbalanced, Lissajous figures appear on the oscillograph screen. Depending on the sign of the slope and the shape of the figure, the resistance of the third arm and the capacity decreases or increases until the ellipse changes into a horizontal straight line which indicates that the bridge is balanced. Having taken the reading of the apparatus, the trap for the water is immersed in a Dewar vessel containing the dry ice—acetone mixture which has a temperature of about −70°, and a MAG-6R electric oven is fitted onto the combustion tube so that it covers the open end of the quartz test tube and the part containing the boat plus sample. Combustion is complete in 3-5 min on moving the oven on to the test tube by hand (in 3-4 stages) or automatically. There is no need to supervise the combustion. During combustion, voltage is not applied to the cell used for measuring the electrical conductivity in order to avoid evolution of Joule heat.

Ten minutes after the first reading, the reading of the apparatus is taken again, tap a is closed, the trap with the frozen water is disconnected and without removing it from the Dewar flask, it is connected into the setup for converting the water (Fig. 2). Usually the water freezes out in the first arm of the U-tube with respect to the direction of the gas flow, so that this arm should be turned towards the system used for purifying the argon on switching from the combustion apparatus to the water conversion apparatus, otherwise during preliminary sweeping of the apparatus with argon some water may be lost. The cell on the water-conversion setup is washed and filled with barium hydroxide solution during the combustion of the aliquot. After connecting up the trap containing water to the water-conversion setup, tap a is set in position I (Fig. 2) for 3-4 minutes and the oxygen is expelled by means of argon passed through the apparatus at the rate of 40-50 ml/min. Tap a is then turned to position II (Fig. 2), and side tap b is slowly opened, the argon being initially passed through the cell at a rate of 25-30 ml/min. When the change in the readings of the apparatus does not exceed 0.1-0.3 ohm per minute, the first reading is taken; the Dewar flask is removed and a vertical tubular oven heated to 300° fitted on to the U-shaped bend of the water trap. The water is evaporated and is carried by the gas stream over a layer of platinized carbon black heated to 900°. The carbon monoxide formed passes with the argon stream into the oxidizing apparatus filled with CuO at 300°, in which carbon monoxide is oxidized to the dioxide. The latter passes into the electrical conductivity cell and is absorbed by the alkali, while the argon passes out into the atmosphere. The reading of the apparatus is taken again after 10 min. When series of determinations are being carried out, combustion of a second aliquot can be carried out while determination of hydrogen is being carried out on the first aliquot in a second setup.

Substances containing C, H, O, and N are analyzed in an empty tube. When sulfur is present, silver is introduced into the tube, while when halogens are present, platinum contacts are also included [24]. Silicon-, phosphorus-, and fluoroorganic compounds are analyzed under the conditions described earlier [25-28]. Mercury does not interfere since it is held back together with water in the trap. Low-boiling liquids to be analyzed are placed in unsealed quartz capillaries [29]. Nitrogen oxides are absorbed outside the combustion tube [21] (Fig. 1d).

Analytical Procedure When 0.01 N Sodium Hydroxide is Used as the Absorbent. In this case there is no need to wash out the cell in between experiments; it is sufficient to run out the used NaOH solution and replace it with fresh solution. The change in resistance (and, accordingly, electrical conductivity) of the solution at the end of an experiment, as the result of the formation of carbonate ions is almost half that in the case where $Ba(OH)_2$ is used, for which, in practice, CO_3^{2-} and HCO_3^{1-} ions are absent in solution.

In practice, when the resistance can be measured with sufficient accuracy, both absorbents can be used, but preference should be given to sodium hydroxide.

Calculations. The percentage content of C and H is determined by means of calibration curves [14] which are constructed on the basis of results of carbon and hydrogen determination by the given method on a series of aliquots of a pure compound (e.g. saccharose) of different weights. The amount of carbon or hydrogen in μg is plotted along the abscissa, while the decrease in electrical conductivity in ohms^{-1} is plotted along the ordinate; this is equal to $1/R_1 - 1/R_2$, where R_1 and R_2 are the initial and final resistances of the absorbent solutions in ohms.

$$\%\,C = \frac{a \cdot 100}{e}; \qquad \%\,H = \frac{b \cdot 100}{e}$$

where a is the amount of carbon in μg found from the calibration curve, b is the amount of hydrogen in μg found from the calibration curve, l is the weight of the aliquot taken in μg.

As an example, calculations for the analysis of benzoic acid are given below.

$$e = 1229\,\gamma.$$

$$R_1^c = 346{,}2\,\text{ohm}\; R_2^c = 406{,}3\ \text{ohm}$$

$$\Delta d_c = 1/346{,}2 - 1/406{,}3 = 427 \times 10^{-6}\ \text{ohm}^{-1}$$

from which, by means of the calibration curve

$$a = 848\,\gamma,\ 848 \cdot 100/1229 = 69{,}02\,\%\ \text{C},$$

$$R_1^H = 373{,}9\ \text{ohm}, R_2^H = 403{,}0\ \text{ohm},$$

$$\Delta d_H = 1/373{,}9 - 1/403{,}0 = 193 \times 10^{-6}\ \text{ohm}^{-1}$$

$$\text{from which } b = 63{,}4,\ \frac{63{,}4 \cdot 100}{1229} = 5{,}16\,\%\ \text{H}.$$

The authors wish to thank N. A. Balashova for valuable advice and hints, and for the interest displayed in this work, and also Yu. S. Solomatin for assembling the electrical apparatus and for constructing the automatically operated oven.

SUMMARY

A method has been developed for the conductometric microdetermination of carbon and hydrogen in organic compounds; it is based on pyrolytic combustion of the test material, freezing out of the water formed, and separate determination of carbon and hydrogen on the basis of the amount of carbon dioxide absorbed by an alkali solution in a cell used for measuring electrical conductivity.

In order to determine hydrogen, use is made of the conversion of water over platinized carbon black in an inert gas stream, whereby the oxygen of the water is converted into carbon monoxide which is oxidized further to carbon dioxide; the latter is then measured conductometrically.

The method opens up possibilities for the automation of all the stages of the analysis, apart from weighing the sample; it is suitable for the analysis of solid and liquid materials containing nitrogen, halogens (including fluorine), sulfur, boron, silicon, phoshorus, and metals.

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ANALYSIS OF MULTICOMPONENT MIXTURES BY MEANS OF INFRARED ABSORPTION SPECTRA

COMMUNICATION 2. DETERMINATION OF CHLOROCUMENE, TERTIARY BUTYLCHLOROBENZENE, AND CHLORODIPHENYLMETHANE ISOMERS*

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The analytical technique used has been described in detail in a previous communication [1]. The work was carried out on a IKS-11 spectrophotometer with cuvettes made from sylvine, and with a layer thickness of 0.09 cm; specially purified carbon disulfide [2] was used as the solvent. Calibration and determination were carried out under the same conditions. Calibration consisted in determining the extinction coefficients of each aromatic compound for each wavelength used.

TABLE 1

Constants of the Test Materials

Test material	Boiling point, °C		Specific gravity		Refractive index		MR	
	found	published values	$d^{20^\circ}_{20^\circ}$	d^{20°	$n^{20^\circ}_D$	$n^{20^\circ}_D$	found	calc.
p-Chlorocumene	191—195	190—195 [4]	1,025	1,026	1,5150	1,5122 [4]	45,4	45,02
o-Chlorocumene	210—214	212—214 [5]	1,037	—	1,5237	—	45,8	45,02
m-Chlorocumene	195—198	—	1,028	—	1,5190	—	45,6	45,02
p-Tertiary butylchlorobenzene	212—215	216 [6]	1,008	1,0075 [6]	1,5122	1,5123 [6]	50,5	49,65
o-Tertiary butylchlorobenzene	210—215	—	1,015	—	1,5140	—	50,0	49,65
m-Tertiary butylchlorobenzene	210—215	—	1,024	—	1,5132	—	49,52	49,65
p-Chlorophenylmethane	147—150 5 mm Hg	162—175 25 mm [7]	1,130	1,128	1,573	—	59,6	60,28
o-Chlorophenylmethane	143—145 4 mm Hg	145—150 5 mm [2]	1,129	—	1,590	—	59,4	60,28
m-Chlorophenylmethane	168—173 25 mm Hg	162—175 25mm [2]	1,162	—	1,588	—	59,4	60,28

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* For Communication 1, see [1].

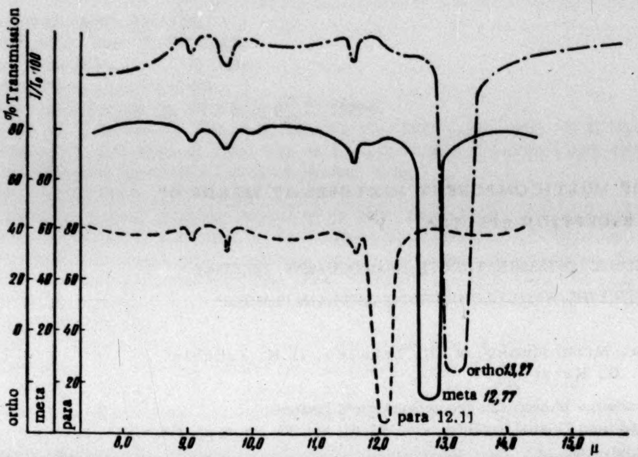

Fig. 1. Absorption spectra of the o-, m-, and p-isomers of chlorocumene. Layer thickness 0.009 cm.

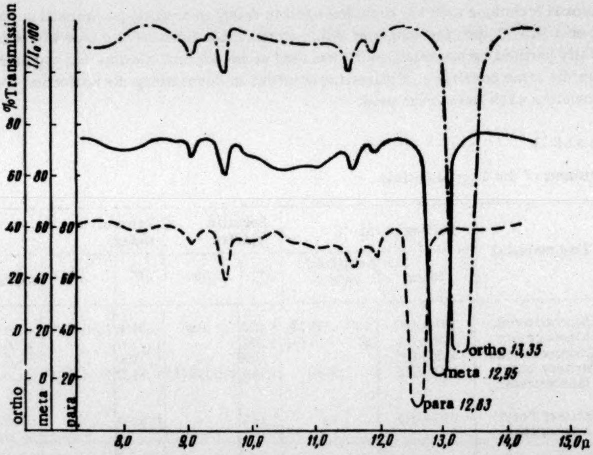

Fig. 2. Absorption spectra of the o-, m-, and p-isomers of tertiary butylchlorobenzene. Layer thickness 0.09 cm.

Ortho-, meta-, and para-isomers of chlorocumene, tertiary butylchlorobenzene, and chlorodiphenylmethane were taken for calibration. The chlorocumene and tertiary butylchlorobenzene isomers were prepared by a Grignard reaction from the corresponding isomer of bromochlorobenzene and alkyl bromide (isopropyl bromide or tertiary butyl bromide). In order to increase the yield of product, n-heptane [3] was used instead of absolute ether as solvent. The chlorodiphenylmethane isomers were prepared by a Friedel-Krafts reaction by condensation of the corresponding isomer of chlorobenzylchloride (obtained by the chlorination of chlorotoluenes at 180-190°) with

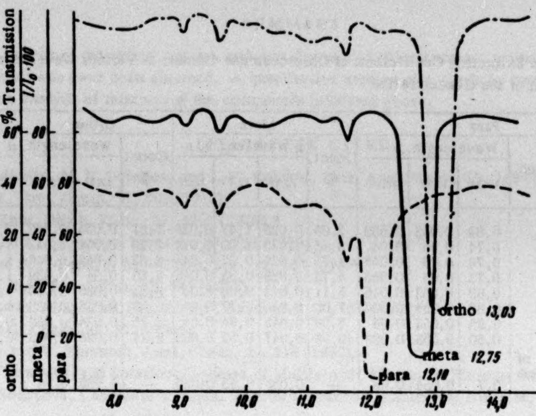

Fig. 3. Absorption spectra of the o-, m-, and p-isomers of chlorophenylmethane. Layer thickness 0.09 cm.

TABLE 2

Values of the Extinction Coefficients of Chlorodiphenylmethane Isomers at Various Wavelengths as a Function of the Concentration

Concentration, %	Para: Wavelength, μ 12,63	Para: 12,95	Para: 13,35	Meta: Conct. %	Meta: Wavelength, μ 12,63	Meta: 12,95	Meta: 13,35	Ortho: Conct. %	Ortho: Wavelength, μ 12,63	Ortho: 12,95	Ortho: 13,35
5,51	0,34	0,018	0,023	—	—	—	—	3,44	0,010	—	1,32
6,22	0,23	0,018	0,024	5,38	0,011	0,83	0,11	4,70	0,011	0,016	1,07
6,41	0,23	0,016	0,026	5,91	0,016	0,76	0,12	5,08	0,011	0,014	1,02
7,42	0,22	0,022	0,025	6,59	0,022	0,74	0,10	5,47	0,021	0,017	1,05
9,43	0,21	0,027	0,026	8,11	0,018	0,63	0,09	6,58	0,022	0,016	0,99
10,72	0,21	0,023	0,026	9,04	0,019	0,61	0,083	6,89	0,033	0,031	0,99
12,49	0,175	0,021	0,028	10,34	0,020	0,60	0,12	8,3	0,03	0,036	0,88
14,88	0,18	0,018	0,027	13,12	0,018	0,52	0,13	11,42	0,026	0,028	0,75
Mean value of the extinction coefficients	0,22	0,021	0,026	—	0,018	0,67	0,11	—	0;026	0,024	1,06

benzene in the presence of aluminum chloride [3]. The constants of the compounds obtained are given in Table 1.

In order to find the absorption maxima for the individual isomers, we first of all carried out a qualitative analysis of all the test compounds. During the search for the absorption bands of individual isomers whose infrared spectra have not yet been described, we used information which has been published in the literature on disubstituted derivatives of benzene, namely, that a band at 13.05-13.55 μ (770-740 cm^{-1}) is characteristic for orthodisubstituted derivatives, while bands at 14.15-14.50 μ (710-690 cm^{-1}) and 12.45-13.05 μ (800-770 cm^{-1}) are characteristic of metadisubstituted derivatives, and a band at 12.00-12.75 μ (833-780 cm^{-1}) [8, 9] is characteristic of paradisubstituted derivatives. The absorption spectra of the isomers of the test chloroalkylbenzenes are given in Figs. 1, 2, 3.

Absorption bands which lie within the limits of the regions for the p-, m-, and o-disubstituted benzenes are observed on the curves we obtained. The following wavelengths proved to be the most suitable ones for the

TABLE 3

Values of the Extinction Coefficients of Chlorocumene Isomers at Various Wavelengths as a Function of the Concentration

Concentration %	Para			Meta				Ortho			
	Wavelength, μ			Conct. %	μ Wavelength, μ			Conct %	Wavelength, μ		
	12,11	12,77	13,27		12,11	12,77	13,27		12,11	12,77	13,27
1,72	0,83	0,053	0,033	2,66	0,025	1,47	0,025	1,81	0,054	0,016	2,00
2,87	0,74	0,06	0,04	3,45	0,023	1,20	0,043	2,23	0,041	0,042	1,93
3,37	0,74	0,06	0,046	4,71	0,021	0,95	0,045	2,32	0,048	0,046	1,90
4,45	0,72	0,05	0,046	4,73	0,023	0,95	0,046	3,65	0,04	0,039	1,30
5,20	0,69	0,053	0,046	5,11	0,042	0,93	0,04	3,85	0,036	0,039	1,25
6,79	0,62	0,054	0,042	7,05	0,04	0,77	0,04	6,58	0,025	0,039	0,76
6,89	0,65	0,054	0,04	8,56	0,045	0,64	0,04	7,25	0,024	0,038	0,69
7,98	0,60	0,053	0,038	10,95	0,047	0,52	0,038	8,24	0,024	0,042	0,61
Mean value of the extinction coefficients	0,7	0,054	0,04	—	0,035	0,93	0,039	—	0,036	0,04	1,30

TABLE 4

Values of the Extinction Coefficients of Tertiary Butylchlorobenzene at Various Wavelengths as a Function of the Concentration

Concentration %	Para			Meta				Ortho			
	Wavelength, μ			Conct. %	Wavelength, μ			Conct. %	Wavelength, μ		
	12,10	12,75	13,03		12,10	12,75	13,03		12,10	12,75	13,03
1,65	0,69	0,05	0,034	2,11	0,018	1,25	0,014	1,89	0,006	0,025	1,88
2,93	0,63	0,059	0,039	3,13	0,041	1,12	0,034	3,42	0,013	0,023	1,25
2,95	0,58	0,053	0,052	3,66	0,039	1,02	0,06	3,74	0,017	0,040	1,18
3,83	0,53	0,039	0,053	4,17	0,044	0,98	0,067	4,25	0,016	0,040	1,11
4,95	0,51	0,036	0,048	4,49	0,061	0,96	0,071	4,73	0,03	0,054	1,02
5,91	0,51	0,035	0,057	5,75	0,057	0,94	0,054	5,27	0,031	0,050	0,95
6,22	0,50	0,043	0,054	8,42	0,049	0,67	0,057	7,30	0,031	0,048	0,69
8,00	0,50	0,038	0,042	9,08	—	0,62	0,05	8,88	0,032	0,042	0,60
Mean value of the extinction coefficients	0,56	0,042	0,047	—	0,043	0,94	0,051	—	0,024	0,04	1,09

determination of the isomers:

o, m, and p-chlorocumene	13.27,	12.77,	12.11 μ,
o, m, and p-tertiary butylchlorobenzenes	13.03,	12.75,	12.10 μ,
o, m, and p-chlorodiphenylmethanes	13.35,	12.95	12.63 μ.

In addition, on the absorption curves, absorption maxima are also observed at 9.64 μ (1037 cm^{-1}) and 9.09 μ (1100 cm^{-1}); these can probably be related to vibrations of the benzene ring [9]([10]?).

Measurements were made of the optical density of each compound in solution in carbon disulfide – at a suitable dilution – for each wavelength chosen, and the extinction coefficients calculated. The results obtained are given in Tables 2, 3, and 4.

Since, during calculation of the composition of mixtures, the Lambert-Beer law is not obeyed, as in the previous paper [1], the method of successive approximation had to be used. An analytical method of calculation had to be used: for the first approximation, the mean values of the extinction coefficients were taken for calculation, while for the second approximation, the values of the coefficients corresponding to the concentrations found in the first approximation, were taken. Results of the analysis of synthetic mixtures showed that the mean relative error is about 4%.

SUMMARY

The infrared spectra of the ortho-, meta-, and para-isomers of chlorocumene, tertiary butylchlorobenzene, and chlorodiphenylmethane have been obtained. A quantitative method of analysis by means of infrared spectra has been used for the analysis of mixtures of the compounds indicated above.

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A SPECTROGRAPHIC METHOD FOR CONTROLLING THE COMPLETENESS OF THE EXTRACTION OF CERTAIN INORGANIC SALTS

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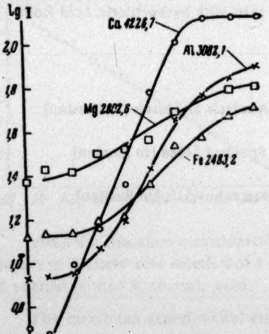
Control of the completeness of extraction of inorganic salts by solvents is carried out fairly frequently in chemical practice. In addition to chemical indicators and radioactive isotopes, etc., which are already in use for this purpose, we should like to suggest an emission spectrographic method in the following form. The residue left after treatment of a cartain material with solvents, and removal of the solution, is analyzed by the "method of additions" which is well known in spectroscopy [1]. The "addition" used in this case is uniformly decreasing amounts of the solution obtained during extraction. The amount of any one of the metals present in solution is taken as unity or as 100%. In this way it is possible to determine the amount of unextracted metal as a fraction or a percentage of the amount of metal which has passed into solution. This serves as a measure of the completeness of extraction.



Curve relating the logarithm of the intensity of the line (log I) and the logarithm of the concentration of the addition (log k). It is arbitrarily assumed that at the origin k = 0(log k = ∞).

The method suggested permits the simultaneous (on the basis of one series of spectrograms) control of completeness of extraction of the salts of all metals. The possibilities of this method are limited solely by the sensitivity of the spectrographic method [2]. In addition, such a technique does not require the use of standards, the preparation of which sometimes, e.g., during the spectrographic determination of rare metals, is a very difficult operation.

We shall clarify what has been said above by taking as an example the determination of the completeness of extraction of Al, Fe, Ca, and Mg salts by hydrochloric acid from clay which has been fused with sodium carbonate [3]. After treating such a melt with hydrochloric acid silicon dioxide should be left undissolved. Salts of the metals indicated should be almost completely extracted into solution. 0.505 g of the dry, washed residue, left after treating with hydrochloric acid, and all the solution obtained, were passed on to the spectrographic laboratory. The dried residue was divided into ten equal parts. To each of these parts was added various amounts of the solution obtained. To the first part, by evaporation and drying to constant weight, were added all the salts dissolved in a tenth part of the solution obtained. The amount of salts returned to each successive part was three times less than that added to the previous part. No solution was added to the last tenth part of the residue. Aliquots (5 mg) of the ten samples prepared in this way were ignited in the crater of a carbon electrode in a dc arc. The spectra were photographed on a ISP-22 spectrograph. The current was 8 amps. Exposure time was 6 min. The sample was placed on the anode. "Spectrographic Type I" plates were used. The following lines were photometrically measured: Al 3082.1; Fe 2483.2; Mg 2802.6; Ca 4246.7. For converting from blackening of the lines to intensity, the marks of nine-stage attenuator were used. Corrections for the background were applied to the intensities. The unknown concentration was then determined graphically by the "method of additions" [1], using the relationship between the intensity of the analytical line "I" of the element and the content of the "addition" of this element k –

$$\log I = b \log (x + k) + a,$$

where $\underline{a}$ and $\underline{b}$ are constants, while $\underline{x}$ is the fraction of unextracted salts of Al, Fe, Ca, and Mg.

On the basis of the values of I found from the spectrograms and the known values of k (k – 100%; 33%; 11%; 3.7%; 1.2%; 0.41%; 0.14%; 0.046%; 0.015%; 0.000%) a curve (log I, log k) was constructed. The straight-line part of the curve which is described by the formula for $x < k$, was extrapolated to $k = 0$, and it was assumed to a first approximation,that the calibration curve can be used for determining $\underline{x}$. From this straight-line part of the calibration curve it was established that concentration $x = x_1$ corresponds to the intensity of the analytical line of the tenth sample, into which no additions have been introduced. Another curve [log I, log $(x_1 + k)$]was then constructed. x_2 was determined from the continuation of the straight-line part of this curve and the line intensity in the tenth sample. x_3, x_4, etc. were determined in the same way. The process of getting more accurate values of $\underline{x}$ was continued until the graph [log I, log $(x_1 + k)$]was linear in the region of low values of $\underline{k}$. In the region of high values of $\underline{k}$, deviation from linearity may even continue on account of the large effect of self-absorption of the lines in the cloud of the arc discharge. The curves (log I, log k) which we obtained for the chosen lines of Al, Fe, Ca, and Mg are shown in the diagram. From these curves we found that when the amount of the elements extracted by hydrochloric acid was taken as 100%, then the amounts remaining in the dry residue after extraction was found to be: Al 0.08 ±0.02%, Fe 0.15 ±0.02%, Ca 0.02 ±0.005%, Mg 0.04 ±0.01%.

SUMMARY

In order to determine the completeness of extraction of inorganic salts by solvents, it has been suggested that the "method of additions" which is well-known in spectroscopy is used for analyzing the insoluble residues. Proportionally decreasing amounts of the solution obtained during the extraction are used as "additions."

As an example, the completeness of the extraction of Al, Fe, Ca, and Mg salts with hydrochloric acid from a clay sample fused with sodium carbonate has been determined.

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PHOTOMETRIC DETERMINATION OF STRONTIUM

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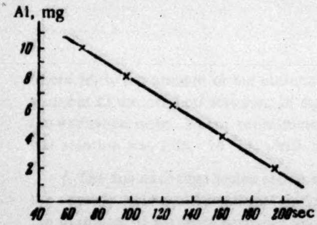
Photometric determination of strontium by means of chloranilic acid [1] possesses a number of essential drawbacks: the precipitation stage is carried out slowly for three hours at the temperature of melting ice. We are unaware of any other photometric methods of determining strontium. We think that it should be possible to use dilituric acid (5-nitrobarbituric or 5-nitro-2,4,6-trihydroxyhexahydropyrimidine) for the photometric determination of strontium, since ions of the latter at room temperature give an insoluble strontium dilituate. The solubility of strontium dilituate at 25° is 1.7 mmoles in 1000 ml [2]. Precipitation of strontium by dilituric acid is complete after 12 min. An aqueous solution of dilituric acid is intense yellow in color; the color decreases in proportion to the amount of strontium precipitated. The change in optical density conforms to Beer's law. Dilituric acid has already been used for the determination of potassium by gravimetric [3], titrimetric [4], and photometric [5] methods.

EXPERIMENTAL

A 0.05 N solution of dilituric acid [6] saturated with strontium dilituate was used for the work.

Equal volumes (5 ml) of the test strontium solution and dilituric acid were taken for precipitation of strontium. The concentration of the test solution varied from 0 to 2 mg Sr/ml, while the dilituric acid concentration was 0.05 N. The mixture of test solution and dilituric acid was carefully mixed and allowed to stand for 15 min. The solution was then filtered and the optical density of the filtrate was measured by means of a Universal Zeiss photometer at 420 mμ (flint-glass prism; layer thickness 0.498 cm; antimony-cesium photoelement MVSB). A calibration curve (Fig.)* was constructed on the basis of the results obtained.



When the strontium concentration of the test solution was greater than 1.75 mg/ml, a ratio of strontium solution to dilituric acid solution of 1 : 1 proved insufficient; in this case it was therefore necessary to increase the volume of 0.05 N dilituric acid.

The maximum experimental error does not exceed 0.02 mg Sr/ml. The mean error of parallel determinations of one sample is ± 0.006 mg Sr/ml. The error is less at higher concentrations. Colorless ions do not interfere with strontium determination; of the cations the following interfere with strontium determination: NH_4, K, Sn, Fe, Cr, Cd, Cu, Ca, Ba, Zn, Co, Ni, Hg, Ag, and Pb.

SUMMARY

Strontium can be determined quantitatively by means of dilituric acid by using a photocolorimeter. When the concentration of strontium in the test solution is less than 1.75 mg/ml, one volume of 0.05 N dilituric acid is taken for one volume of the test solution. At higher strontium concentrations the quantity of dilituric acid must

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*The Fig. shown is the one appearing in the Russian original, and does not appear to be the correct one.

be increased proportionally.

When low concentrations are determined the maximum error does not exceed 2%. The error decreases with increasing concentration.

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SEPARATION OF TITANIUM FROM MANGANESE BY ION EXCHANGE CHROMATOGRAPHY

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Chromatographic methods have been developed for the separation of titanium from iron [1-2], aluminum [3-5], vanadium [6], zirconium and thorium [7], and tungsten, niobium, and molybdenum [8]. We have studied the possibility of separating titanium from manganese by means of ion exchange resins from hydrochloric acid solutions with HCl concentrations ranging from 0.1 to 10 N.

The partition coefficients of quadrivalent titanium and divalent manganese between ion exchange resins and hydrochloric acid solutions were determined by the method of Alimarin, Belyavskaya, and Bazhanova, which was modified slightly: an accurately known amount of the air-dry ion exchange resin was shaken with a known volume of test solution until equilibrium had been reached; aliquots of the solutions were then taken and the amount of manganese in the form MnO_4^-, not sorbed by the resin, and titanium in the form $[Ti(H_2O_2)]^{2+}$, not sorbed by the resin, determined photometrically [9]. The partition coefficients were determined by means of the formula:

$$\varphi = \frac{M_1}{M - M_1} \cdot \frac{v}{m},$$

where M_1 is the amount of the element sorbed by the ion exchange resin, in mg; M is the total amount of the element in the original solution, in mg; v is the volume of solution used in the experiment; m is the weight of ion exchange resin. In our experiments v = 50 ml and m = 0.5 g. The concentration of the original titanium salt solution was $2.50 \cdot 10^{-3}$M, while that of the manganese salt solution was $5.03 \cdot 10^{-3}$M.

The ion exchange resins tested were the strongly acid, unifunctional cation exchange resins KU-2 and SBS, the strongly acid multifunctional cation exchange resin KU-1, and the anion exchange resin AN-2F. In all cases the diameter of the resin particles was 0.5-1.0 mm. Prior to use the resins were washed free from impurities, while the cation exchange resins were converted into the H-form and the anion exchange resin into the Cl-form. Results of the determination of the partition coefficients are given in Table 1.

Titanium was found to be sorbed to a greater extent than manganese by all the cation exchange resins from 0.1-1 N hydrochloric acid solutions. The sorbability of both elements rapidly decreased, but to different extents, with increasing acidity. From the ratios of the partition coefficients, it is reasonable to assume that manganese can be separated from titanium by means of the cation exchange resin KU-1 at 0.5 N HCl.

In order to check on this assumption we carried out the following experiments. Columns 10 cm long and 1 cm in diameter were filled with KU-1 cation exchange resin in the H-form, the resin was washed with 0.5 N hydrochloric acid, and the test solutions (0.5 N with respect to hydrochloric acid) containing titanium and manganese in varying weight proportions introduced onto the column. The columns were then washed with 0.5 N hydrochloric acid until all the manganese had been eluted; the elution rate was 30 drops per minute. In order to speed up elution of titanium, 4 N rather than 2 N hydrochloric acid was used.

TABLE 1

Partition Coefficients of Titanium and Manganese between Hydrochloric Acid Solutions and Ion Exchange Resins

HCl concentration, M	φTi	φMn	φTi/φMn	HCl concentration, M	φTi	φMn	φTi/φMn
Cation exchange resin KU-1				Cation exchange resin KU-2			
0,1	344,48	48,93	7,04	0,1	324,61	292,96	1,11
0,5	20,68	2,19	9,44	0,5	22,47	22,45	1,00
1	2,22	0	—	1	1,95	0	—
2	0	0	—	2	0	0	—
4	0	0	—	4	0	0	—
8	0	0	—	8	0	0	—
Cation exchange resin SBS				Anion exchange resin AN-2F			
0,1	156,26	72,46	2,16	0,1	0	0	—
0,5	30,49	14,79	2,06	0,5	0	0	—
1	0	0	—	1	0	0	—
2	0	0	—	2	0	0	—
4	0	0	—	4	0	0	—
8	0	0	—	8	14,76	0	—
				10	108,42	0	—

TABLE 2

Separation of Titanium and Manganese on KU-1 from Hydrochloric Acid Solutions

Weight ratio Mn:Ti	Mn taken mg	Volume of 0.5 N HCl used for eluting the magnanese, ml	Mn found mg	Ti taken mg	Volume of 4 N HCl used for eluting the titanium, ml	Ti found, mg
1 : 1000	0,0050	150	0,0048	5,0000	150	4,9825
1 : 1000	0,0050	150	0,0048	5,0000	150	4,9785
1 : 1	0,0050	150	0,0049	0,0050	100	0,0049
1 : 1	0,0050	150	0,0049	0,0050	100	0,0048
1000 : 1	5,0000	200	4,9285	0,0050	100	0,0048
1000 : 1	5,0000	200	4,8570	0,0050	100	0,0049

It is clear from Table 2 that the suggested method for separating titanium and manganese gives satisfactory results, and can be used for quantitative analysis.

The drop in the sorbability of the test elements which is observed on increasing the acidity of the solutions cannot be explained simply by the change in hydrogen ion concentration. It is clear from Table 1 that, starting at 8 N HCl, titanium is sorbed by the anion exchange resion AN-2F, and consequently changes into an anionic complex; this is not observed in the case of manganese. Formation of anionic complexes by titanium in sufficiently concentrated hydrochloric acid solutions has already been used for separating this element from other elements by means of anion exchange resins [10]. Presumably, this property can also be used for separating titanium from manganese.

SUMMARY

The partition coefficients of titanium and manganese ions between the cation exchange resins KU-1, KU-2 and SBS and hydrochloric acid solutions (0.1 to 10 N HCl) have been studied. A method has been developed for the quantitative separation of titanium from manganese in hydrochloric acid solutions by means of the cation exchange resin KU-1 for ratios of Ti : Mn ranging from 1 : 1000 to 1000 : 1. It has been established that, starting at 8 N HCl, titanium forms anionic complexes.

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* Original Russian pagination. See C. B. translation.

ORGANIC REAGENTS FOR OSMIUM

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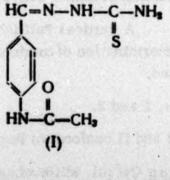
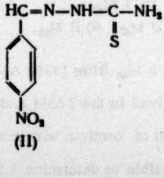
L. Chugaev [1] has shown that on heating solutions containing osmium in the form of OsO_4 or chlorosmiate in the presence of thiourea and several drops of HCl for several minutes, a red color appears as the result of the formation of the compound $[Os(H_2N-CS-NH_2)_6]Cl_3 \cdot H_2O$. This reaction has been used by Sandell [2] for the photometric determination of traces of osmium in meteorites, Steiger [3], during a study of the interaction of 21 derivatives of thiourea $(R_2N)_2CS$ with osmium and ruthenium compounds, showed that formation of the colored compounds is determined by the group >Cs, connected with one or two radicals $-NH_2$ or -NHP. Yoe and Overholser [4] qualitatively studied the interaction of 60 thiourea derivatives with 78 inorganic ions, including osmium and ruthenium. Bardoděj [5] as a result of a study of various organic materials as reagents, concluded that the group >CS is a functional analytical group of Os and Ru. He established that OsO_4 gives a red color with $(H_2N)_2CS$; $CS(NHC_6H_5)_2$ and $H_2NCSNHNH_2$; and a violet color with $H_2NCSNHC_6H_5$; $CS(NHCH_3)_2$; $SC[N(CH_3)_2]_2$; NH_4SCN and $NaCSN(C_2H_5)_2$.

The aim of the work described here was a study of the interaction of osmium compounds with two substituted thiourea derivatives: 4-acetylaminobenzaldehydethiosemicarbazone (I) and 4-nitrobenzaldehydethiosemicarbazone (II)



(I)



(II)

Compound I is used for the cure of tuberculosis under the name tebezon or TB_1.

A solution of OsO_4 obtained by dissolving 1 g OsO_4 in 100 ml 0.2 M NaOH was used in the work. It was standardized by Klobbie's method [6]. The Os content of the solution was 49.12 μg Os / ml.

Reagent I was used as a 0.1% solution in 1% NaOH, reagent II as a 0.05% solution in 1% NaOH. Both reagents were used in the form of freshly prepared solutions.

From 0.1 to 3 ml of the osmium solution was placed in a standard flask (10 ml), and 1 ml of H_2SO_4 added (obtained by mixing 32 ml of concentrated H_2SO_4 and 68 ml of H_2O). Two ml of the reagent solution was then added and the final solution allowed to stand for 5 min in the case of reagent I, and 15 minutes in the case of reagent II. Control solutions containing the same amounts of reagents were prepared in parallel.

Under the conditions indicated, osmium formed with reagent I a brown-colored precipitate, which dissolved on adding ethanol to the mark; a yellow-brown solution was thereby obtained depending on the osmium concentra-

Os, µg/ml	Optical density with various filters from a Pulfrich photometer					
	Reagent I			Reagent II		
	M_{43}	M_{47}	M_{50}	M_{43}	M_{47}	M_{50}
4,9	—	—	—	0,05	0,04	0,04
12,3	0,08	0,06	0,045	0,125	0,11	0,09
24,6	0,16	0,12	0,09	0,245	0,21	0,17
49,1	0,32	0,24	0,18	0,49	0,42	0,34
73,7	—	—	—	0,73	0,63	0,51
86,0	—	—	—	0,855	0,74	0,60
98,2	0,64	0,48	0,36	—	—	—
122,8	0,80	0,60	0,45	—	—	—
147,4	0,96	0,72	0,54	—	—	—

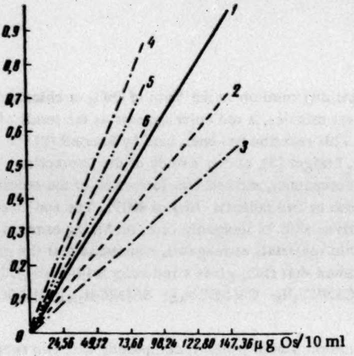


Fig. 1. Conformation of solutions of the compounds of osmium with reagents I and II to Beer's law. 1) I M_{43}; 2) I M_{47}; 3) I M_{50}; 4) II M_{43}; 5) II M_{47}; 6) II M_{50}.

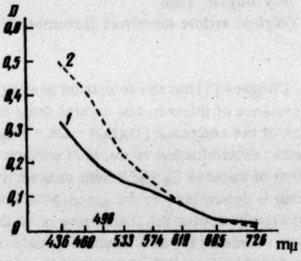


Fig. 2. Absorption curves of the compounds of osmium with reagents I and II. 1) Reagent I, 49.12 Os/10 ml; 2) Reagent II, 49.12 Os/10 ml.

tion. A red-brown color was obtained on diluting the solution obtained with reagent II with alcohol.

A vertical Pulfrich photometer was used for the determination of osmium. The maximum optical density was observed in both cases when a M_{43} filter (4360 A) was used.

The results obtained are given in the Table and in Figs. 1 and 2.

Solutions of the compounds of osmium with reagents I and II conform to Beer's law.

By using reagent I it is possible to determine 1.2-14.7 µg Os/ml, while when reagent II is used it is possible to determine 0.49-8.60 µg Os/ml. Both reagents are more sensitive than thiourea, which only permits determination of 8-40 µg Os/ml. The higher sensitivity of detection of osmium with reagent II can be explained by the influence of the nitro group, which leads to an increase in the polarity of the group in the para position.

SUMMARY

4-Acetylaminobenzaldehydethiosemicarbazone (I) and 4-nitrobenzaldehydethiosemicarbazone (II) are suggested as reagents for the photometric determination of osmium. They permit the determination of 1.2 to 14.7 µg Os/ml and 0.49 to 8.60 µg Os/ml, respectively. Both reagents are more sensitive than thiourea.

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REDUCTION OF QUADRIVALENT SELENIUM WITH L-ASCORBIC ACID

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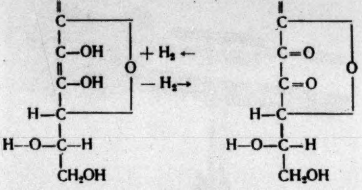
L-ascorbic, D-ascorbic, D-araboascorbic, and other acids are known. L-ascorbic acid is the lactone of 2,3-dienol-L-gulonic acid. Its molecular weight is 176.12 while its melting point is 190-192°. It is readily soluble in water and alcohol but insoluble in ether. Since the dienol group $-C(OH)=C(OH)-$ enters into its composition, it possesses reducing properties, and on being oxidized is converted into dehydroascorbic acid, which is not such a strong reducing agent, and accordingly only interacts weakly with oxidizing agents. Conversion of L-ascorbic acid (I) into dehydroascorbic acid (II) can be represented by the following equation:



I II

The reducing properties of L-ascorbic acid are used comparatively little in analytical chemistry. Below are given the results of a study of the reduction of quadrivalent selenium in an acid medium.

L-ascorbic acid precipitates elemental selenium from solutions of selenites. The reaction is very sensitive and can be successfully used for the detection and determination of selenium in the presence of tellurium, and also for the detection and determination of ascorbic acid. When a dilute solution of L-ascorbic acid (0.1-1 mg in 1 ml) is added to an aqueous solution of a selenite, an orange-colored precipitate of elemental selenium separates out almost immediately. In the presence of mineral acids, and on heating, the reduction is speeded up appreciably. The sensitivity of the detection of selenium is 0.01 mg in 1 ml of solution. The sensitivity of the detection of ascorbic acid is 0.008 mg in 1 ml of solution. Solutions of the salts of zinc, cadmium, lead, bismuth, manganese, chromium, aluminum, divalent mercury, nickel, cobalt, the alkali and alkaline earth elements, and also dilute solutions of copper, silver, univalent mercury, and trivalent iron (the red-violet color formed disappears on adding excess of the reagent) salts do not interfere. Solutions of quadrivalent tellurium salts do not interfere either. The fact is that salts of quadrivalent tellurium only interact with relatively concentrated solutions of ascorbic acid (concentrations greater than 1 mg/ml). The presence of oxidizing agents does not essentially affect reduction of quadrivalent selenium; it is only necessary to use excess of the reagent. Reducing agents: iodides, thiocyanates, sulfides, sulfites, stannous chloride, divalent iron, thiourea, etc., interfere.

The interaction of L-ascorbic acid with quadrivalent selenium presumably proceeds according to the following equation:

$$2C_6H_8O_6 + Me_2SeO_3 \rightarrow 2C_6H_6O_6 + Se + 2MeOH + H_2O.$$

One gram of selenium corresponds to 4.4609 g of L-ascorbic acid. Reduction proceeds quantitatively. Thus, 0.3390 g and 0.4560 g of selenium was taken in the form of a selenite, and 0.3388 and 0.4568 g of selenium was obtained. Selenium is precipitated most completely from selenites at a pH of 1. For this purpose a 2 molar solution of sulfuric acid (1 ml of acid for 2 ml of reaction mixture) should be added to the reaction mixture. Heating to 80-90° also favors the reduction. On boiling, the orange-colored selenium changes to a black-brown modification which is readily removed from the liquid. Sometimes it accumulates in the form of lumps, which can be weighed after drying.

The results given above indicate that it is possible to detect and determine selenium in the presence of tellurium and a number of other metals by means of ascorbic acid. Ascorbic acid has a number of advantages over other reducing agents for quadrivalent selenium. Under certain conditions it reduces quadrivalent selenium, while leaving tellurium compounds unchanged.

SUMMARY

L-ascorbic acid can be used in acid media for the detection and determination of selenium in the presence of tellurium and other metals.

A SPECTROGRAPHIC METHOD FOR THE DETERMINATION OF PHOSPHORUS IN BERYLLIUM OXIDE

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Methods have been described for the spectrographic control of the purity of beryllium and its oxide [1-3]. Phosphorus has, however, not been determined spectrographically. When the test material is packed into the carbon electrodes it is only possible to determine down to 0.03% P. We have developed a method which permits the determination of down to 0.001% phosphorus in beryllium oxide without preliminary enrichment.

The powdered sample of beryllium oxide is diluted with carbon powder in the proportion of 3 : 1, and, using a solution of collodion in ethanol, the sample is attached to the lateral faces of graphite cylinders 40 mm in diameter and 80 mm long, after which the latter are dried at 100-150° for 15-20 min. The graphite cylinders with the samples attached to them (lower electrodes) are fixed in a special gadget for introducing samples into the light source (Fig. 1). Using an electric motor of the SD-2 type, the cylindrical electrode is brought into a forward rotational movement along a guiding axis with a screw thread. The rate at which the electrode rotates is 1 rpm, the pitch of the screw being 0.5 cm. The linear rate at which the electrode surface moves under these conditions is equal to 0.2 cm/sec. The upper electrode is a carbon rod with a diameter of 6 mm. The distance between the electrodes is 2 mm.

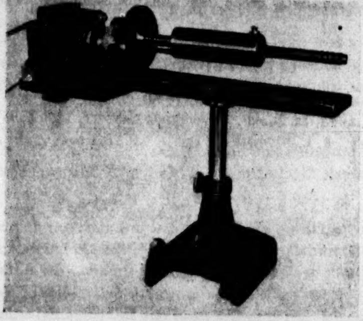

Fig. 1.

The spectra are photographed on an ISP-22 spectrograph. The slit width of the spectrograph is 0.02 mm. The light source is an ordinary ac arc supplied from a DG-1 generator with an interruptor. The current strength is 14 amps. The burning time and the break time are 0.5 sec each. Total exposure time is 3 min. The light source is focused on the collimator mirror by means of a three-lens condensor system.

Spectrographic photographic plates type III which have been sensitized by a 20% solution of sodium salicylate in 50% aqueous alcohol, are used. The plates are immersed in the solution for 3 sec and dried for 2-3 min with an air stream. The plates are developed in a No. 1 metolhydroquinone developer made up according to NIKFI, and are fixed in an acid fixer. The sodium salicylate is not removed prior to development. The spectrograms are measured photometrically on a MF-2 microphotometer.

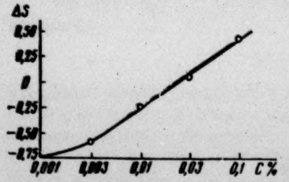

Fig. 2.

Standards containing from 0.001 to 0.1% phosphorus are prepared by grinding up calcium phosphate $Ca_3(PO_4)_2$ with pure beryllium oxide. Pure beryllium oxide is prepared by calcining beryllium carbonate $BeCO_3 \cdot Be(OH)_2$ at 700-800° for 1 hour. 3% of Bi_2O_3 is introduced as an internal standard into all the standards and into the test samples.

The analytical pair of lines used are: P_I 2136.2 and Bi_I 2133.6. Calibration curves are constructed within the coordinates (log C, ΔS) where C is the phosphorus concentration in the standards, ΔS is the difference in blackening of the analytical pair of lines (Fig. 2).

The sensitivity of the determination of phosphorus in beryllium oxides by means of the method described is 0.001%. The reproducibility of the analytical results within the concentration range 0.005-0.1% is ± 5-6%, while at concentrations less than 0.005% the reproducibility drops to ± 10-15%.

SUMMARY

A technique has been developed for the spectrographic determination of small amounts of phosphorus in beryllium oxide. An ordinary ac arc is used as the light source. The sample is introduced into the light source on a moving graphite electrode. The sensitivity of the determination is 0.001%. The reproducibility of the results is ±5-6%.

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* Original Russian pagination. See C. B. translation.

RAPID DETECTION OF FLUORINE IN ORGANIC FLUORINE CONTAINING MATERIALS BY NONWETTABILITY OF GLASS

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Fetkenheuer [1] discovered that glass is not wetted by sulfuric acid in the presence of inorganic fluorides. In 1934 Hagen [2] used this phenomenon for the detection of fluorine in inorganic fluorides. Dubnikov and Tikhomirov [3] while studying the applicability of this method to inorganic fluroides, suggested a suitable design for the reaction tube and established the relation of the limit of detection and many factors. In order to detect fluorine a chromic mixture is first introduced into a J-shaped tube in order to ensure that the glass is readily wetted; one drop of the fluoride is then added. When sufficient fluorine is present the chromic acid ceases to wet the tube walls. The advantagesof the method are its simplicity, specificity, and the rapidity with which fluorine can be detected in small amounts of material. Canneri and Cozzi [4] were the first to use this method for the quantitative determination of fluorine in inorganic fluorides from the change in the wetting angle.

Detection of fluorine in organic fluorine-containing materials by means of this method has not been studied. Dubnikov and Tikhomirov [3] only carried out preliminary investigations on this question. They concluded that, in principle, this method could be used for this purpose, but pointed out that this question should be specially studied. However, Vaibel [5] recommending this method as a basis, writes "The presence of fluorine can be established in organic materials as well as in inorganic materials." As a basis for his conclusion he refers to Hagen's work [2], who, however, did not study organic fluorine-containing materials. This conclusion is equivalent to affirming that chromic acid can split the C—F bond in all materials. Naturally, this is a point that must be checked.

In the work described here an investigation was made of the possibility of detecting fluorine in small amounts of organic fluorine-containing materials on the basis of the nonwettability of glass. The extension of this method to organic materials is very tempting. In the usual methods of detecting fluorine in organic compounds it is necessary first of all to mineralize the compound in order to break the C—F bond. This almost invariably requires fairly complicated apparatus and takes a long time. Moreover, in order to detect fluorine, it is often necessary to separate it from interfering impurities. Detection of fluorine in organic materials on the basis of the nonwettability of glass would give the possibility of mineralizing the test material and detecting fluorine in it on the same sample rapidly and simply.

In order to devise a more accurate procedure a preliminary study was made (on chemically pure sodium fluoride, recrystallized twice according to Tananaev's method [6]) of the relation between the limit of identification and the concentration of sulfuric acid and potassium dichromate, the volume of the chromic mixture, and the temperature.

It has been established previously [3] that the limit of identification depends on the composition of the silicate glass and on the diameter of the tube. In a tube made of quartz glass it is possible to detect 0.2 μg of fluorine in a drop, while in tubes made of glass containing 20% B_2O_3 or 25% Al_2O_3, 0.5 μg of fluorine can be

TABLE 1

Limit of Identification of Fluorine in One Drop from the Non-wettability of Glass when the Material is Mineralized with a Solution of $K_2Cr_2O_7$ in Oleum ("+" is a positive, "−" is a negative result; t signifies that the test was carried out with heating).

Test material	Without the solvent	Aqueous solution containing μg F in a drop					Alcoholic solution containing μg F in a drop				Ethereal solution containing μg F in a drop		
		20	10	5	2	1	1 %	50 γ	20 γ	10 γ	100	50	20
$FC_2H_4N(C_2H_4)_2O$	+	+ t	+ t	+ t	−	−	+	−	−	−	Insoluble		
$FC_2H_4N(C_2H_4)_2S$	+	Insoluble					+	−	−	−	+	−	−
F_3CCOOH	−	−	−	−	−	−	−	−	−	−	Insoluble		
FCH_2COOH	+ t	+ t	+ t	−	−	−	+ t	−	−	−	Insoluble		
FCN_2CHOCH_2	+	+	+	+ t	−	−	+	+	+	−	+	+ t	−
C_6H_5COF	+	+ Insoluble but hydrolyzes										+	−
	t	t	−	−	−	−	+	+	+	−	+	t	
$C_6H_5SO_2F$	+	+	+	+ t	−	−	+	+	+	−	+	+ t	+ t
CCl_2FCF_2Cl	−	Insoluble					−	−	−	−	−	−	−
$(CCl_2F)_2$	−	The same					−	−	−	−	−	−	−
$CCl_2F\ SCH_2CHClCH_2Cl$	+ t	The same					+ t	+ t	−	−	+	−	−
$(FCH_2CH_2O)_3PO$	+	The same					+ t	+	−	−	+ t After 2 hours	−	−
$(FCH_2CH_2O)_3P$	+	The same					+ t	−	−	−	+ t After 2 hours		

detected. In a tube with a diameter of 5 mm, 0.4 μg of fluorine can be detected, while in a tube of diameter 10 mm, only 1 μg of fluorine can be detected, and in a 15 mm diameter tube only 10 μg of fluorine can be detected in one drop. Experiments were carried out in tubes made of mark Ts-32 glass from the Klinskii factory, the diameter being 5 mm. The limit of identification of fluorine in these tubes is 0.25 μg fluorine in a drop.

The limit of identification depends on the acid concentration. The following strengths of sulfuric acid were used: 75%, 100%, and oleum containing 10% sulfur trioxide. It was established that all these acids can be used when 2 μg of fluorine or more is present in a drop. One μg of fluorine can be detected in a drop when 100% sulfuric acid or oleum is used, while 0.25 μg of fluorine can only be detected when oleum is used.

The potassium dichromate concentration does not affect the limit of identification, but shows up the non-wettability of the glass more clearly on account of the increase in color of the solution.

The limit of identification depends on the volume of the chromic mixture. 0.25 μg fluorine cannot be detected in one drop either in a small (0.2-0.3 ml) or in a large (2 ml and more) volume of chromic mixture. The optimum volume is 0.5-1 ml.

TABLE 2

Limit of Identification of Fluorine in a Drop of an Alcoholic Solution of the Organic Materials, from the Nonwettability of Glass, when the Material was Mineralized with a Solution of $K_2Cr_2O_7$ in Oleum ("+" is a positive, and "−" is a negative result).

Test material	Alcoholic solution containing F in a drop			
	1 %	50 γ	20 γ	10 γ
$C_6H_5SCF_2CF_2H$	+	−	−	−
$CH_2ClCH_2SCF_2CFClH$	−	−	−	−
$O_2NCFCClCF_2NO_2$	−	−	−	−
O_2NCF_2COOH	+	+	−	−
$CF_3CF(NO_2)COOH$	+ t	−	−	−

The limit of identification depends on the temperature. The optimum experimental temperature is 15-50°. Both at low temperatures (about 0°) and at high temperatures (about 100°) it is only possible to detect 1-2 μg fluorine reliably, instead of 0.25 μg fluorine, which can be detected at the optimum temperature.

The limit of identification of fluorine in inorganic fluorides is independent of the nature of the oxidizing agent (dichromate or permanganate). Replacement of dichromate by permanganate improves the mineralization conditions of fluorine-containing materials on account of the higher oxidation−reduction potential of potassium permanganate.

Procedure. Into a J-shaped tube made from mark Ts-32 glass from the Klinskii factory, the diameter of the tube being 5 mm, was introduced 0.7 ml of a 4% solution of $K_2Cr_2O_7$ in oleum (or a 2% solution of potassium permanganate). By alternate shaking of the tube the glass surface was cleaned until it was readily wetted by the oleum. Into the short arm of the tube, at room temperature, was introduced one drop of the fluorine-containing material or its solution. The sample was mixed by shaking the tube. When 1 μg and more of fluorine was present in the drop, then on inclining the long arm of the tube downwards, the film of the liquid in the short arm immediately crept without wetting the glass. When smaller amounts of fluorine were present, this nonwettability was only manifested after several minutes. In some cases, when a negative result was obtained, the tube was heated to 50°. The values taken were the results of three parallel determinations.

In order to carry out the experiments 17 organic compounds with different fluorine-carbon groups were taken: C'OF, CF_3, CF_2, CF, CFCl; the compounds were sufficiently analytically pure. Twelve of these were tested in the free state (i.e., without using a solvent), 17 in alcoholic solution, 9 in ethereal solution, and 6 in aqueous solutions.

The limit of identification of fluorine in organic fluorine-containing compounds when they were mineralized with a chromic mixture ($K_2Cr_2O_7$ in 10% oleum) is given in Table 1. Table 2 contains the limit of identification for some materials used only in alcoholic solutions.

When chromic acid was used for mineralizing organic compounds containing CF_3 or fluorochloride groups, flourine could not be detected from the nonwettability of glass, either when the pure materials or their solutions were used. Fluorine could be detected by this method in organic fluorine-containing materials with the C−F group, both in the pure materials and in their solutions, but in some cases a positive result was only obtained when the mixture was heated. In aqueous solutions of materials containing the CF_2 and CF groups it was found possible to detect 10-20 μg of fluorine in one drop. In alcoholic solutions of individual materials it was found possible to detect 20-50 μg fluorine in one drop and 1% of fluorine in a drop of each material. 100 μg of fluorine could be detected in a drop of the ethereal solutions. Fluorine was most easily detected from the nonwettability of glass in fluoroanhydrides.

The conclusion can therefore be made that detection of fluorine in organic fluorine-containing materials by the procedure used for inorganic fluorides can only be successfully carried out when the molecule of the test material contains a readily mobile fluorine atom. This is related to the difficulty of splitting the C−F bond with a chromic mixture. It was found possible to increase the sensitivity of detection by using a solution of $KMnO_4$ in oleum for mineralizing the material.

The limit of identification of fluorine in organic fluorine-containing materials when a solution of $KMnO_4$ in oleum is used for mineralizing them is given in Table 3. The limits of identification for several materials taken only in alcoholic solutions are given in Table 4.

TABLE 3

Limit of Identification of Fluorine in a Drop of Test Organic Materials, from the Nonwettability of Glass, when the Materials were Mineralized with a Solution of $KMnO_4$ in Oleum ("+" is a positive, and "−" is a negative result)

Test material	In the absence of a solvent	Aqueous solutions containing μg F in a drop					Alcoholic solutions containing μg or % F in a drop				Ethereal solutions containing μg F in a drop		
		20	10	5	2	1	1 %	50 γ	20 γ	10 γ	100	50	20
$FC_2H_4N(C_2H_4)_2O$	+	+	+	+	+	+	+	+	−	−	Insoluble		
$FC_2H_4N(C_2H_4)_2S$	+	Insoluble					+	+	−	−	+	−	−
F_3CCOOH	+	+	+	−	−	−	+	+	−	−	Insoluble		
FCH_2COOH	+	+	+	+	−	−	+	+	+	−	the same		
FCH_2CHOCH_3	+	+	+	+	+	−	+	+	+	−	+	−	−
C_2H_5COF	+	+ Insoluble but hydrolyzes	+	+	+	+	+	+	+	−	+	+	−
$C_2H_5SO_2F$	+	+	+	+	+	+	+	+	+	−	+	+	−
CCl_2FCF_2Cl	+ After 3 hours	Insoluble					−	−	−	−	−	−	−
$(CCl_2F)_2$	+ After 4 hours	the same					−	−	−	−	−	−	−
$CCl_2FSCH_2CHClCH_2Cl$	+	the same					+	+	−	−	+	+	−
$(FCH_2CH_2O)_3PO$	+	the same					+	−	−	−	+	−	−
$(FCH_2CH_2O_3)P$	+	the same					+	−	−	−	+	−	−

TABLE 4

Limit of Identification of Fluorine in a Drop of the Alcoholic Solutions of Test Materials, from the Nonwettability of Glass, when Mineralization was Carried out with a Solution of $KMnO_4$ in Oleum ("+" is a positive, "−" is a negative result)

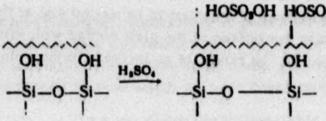
Test material	Alcoholic solutions containing μg or %F in a drop			
	1 %	50 γ	20 γ	10 γ
$C_6H_5SCF_2CF_2H$	+	+	+	−
$CH_2ClCH_2SCF_2CFClH$	+	+	+	−
$O_2NCFClCF_2NO_2$	+	−	−	−
O_2NCF_2COOH	+	+	+	−
$CF_3CF(NO_2)COOH$	+	−	−	−

When potassium permanganate in oleum was used for mineralization, fluorine was detected in a drop of each of 12 materials taken neat, even in fluorochlorides and in compounds containing the CF_3 group. As before, the most difficult compounds to mineralize were carbon fluorochlorides. Fluorine could only be detected in these after a three-hour interaction.

5-10 μg of fluorine could be detected reliably in a drop of the aqueous solutions of all the test materials, and, even 1-2 μg in some cases. In alcoholic solutions 50 μg of fluorine could be detected, and, in some cases, 20 μg. In ethereal solutions 100 μg of fluorine could be detected. Fluorine could not be detected in solutions of fluorochlorohydrocarbons by this method.

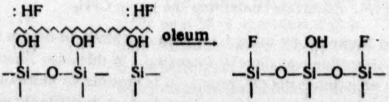
The Probable Mechanism of the Process. The nonwetting phenomenon is determined by the interaction of the HF formed during the reaction, with the silicate glass. Under these conditions the following may be formed on the glass surface: a film of SiF_4; crystals of silicon fluorides and metal fluorides; surface fluoride compounds. Earlier [3] it was shown that no SiF_4 films are present on the glass surface; this eliminates one of the possible reasons for the nonwettability of glass. Formation of metal fluorides and silicofluorides, under conditions where only low amounts of fluorine are present, is of low probability. In addition, formation of these compounds does not appear to be the reason why the glass is not wetted; this follows from a fact which we established, namely, that the same phenomenon is observed on quartz glass. The most probable reason therefore for the nonwetting of glass is the appearance on the glass surface of fluoride compounds.

It is known [7-9] that the surface of silica gel and silicates is completely or partially covered by hydroxyl groups. It might be assumed that wetting of such a surface occurs as the result of adsorption of materials by means of hydrogen bonds:



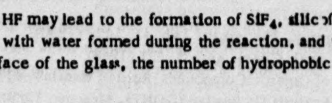
It has been established that OH groups can enter into exchange reactions [10].

The first stage of the process can be regarded as being the adsorption of HF by the hydroxyl groups of the surface. Subsequently, in the presence of oleum, water is split off, and a hydrophobic surface fluoride compounds are formed:



Such a surface having the groups SiOH and SiF loses its capacity to be wetted. On this surface a liquid flows off the hydrophobic parts onto the hydrophilic parts. When such parts are formed on alternating parts of the surface and they assume a certain size, continuous movement of the liquid is observed, i.e., the liquid will creep. The nonwetting of glass, whose surface is partially occupied by paraffin, was explained by Aron [11] in the same way, as the result of alternation of hydrophobic and hydrophilic parts.

The further action of excess HF may lead to the formation of SiF_4, silicofluorides, and metal fluorides on the glass surface. SiF_4 reacts both with water formed during the reaction, and with metal fluorides. As a result of the formation of SiF_4 on the surface of the glass, the number of hydrophobic parts decreases and parts become hydrophilic.



Such a surface should be wetted by sulfuric acid.

In order to clarify the problem as to the possibility of increasing the number of hydrophilic parts on the surface during the course of the reaction, a reaction tube was placed in a 0.5% solution of KFHF and tests carried out over a period of 24 hours for the phenomenon of nonwetting. In the course of 16 hours it was observed that the the tube was not wetted by the chromic mixture; subsequently the tube was wetted by the mixture. This to some extent confirms that the mechanism suggested is probably correct. This mechanism was also confirmed in experiments on glass with the electron microscope, carried out at our request by Luk'yanovich. He studied (at a magnification of 15,000) the surface of glass: a) not treated with HF; b) treated with HF until the glass had a mat finish; and c) treated with HF containing 50 μg F in a drop. On the surface of glass plates which had either not been treated with HF, or had been treated with concentrated HF, no changes were observed. On the surface of plates which had been etched with HF whose concentration was 50 μg F in a drop, no changes visible to the naked eye could be detected, but under the electron microscope the surface proved to be completely covered by mounds of irregular form, with dimensions ranging from 200 to 1000 A.

This probable mechanism of the process explains a number of phenomena which have been observed. The existence of an optimum reaction temperature is connected with the fact that changes in temperature affect both the adsorption of HF and the rate of the reaction with the glass. Increasing the temperature leads to a decrease in the amount of HF adsorbed, while a decrease in temperature slows down the reaction rate. The sulfuric acid concentration affects its capacity to bind the water formed during the reaction. According to our results, the use of oleum instead of 75% sulfuric acid increases the limit of identification 8-10 times. An optimum value of reaction mixture is necessary because an increase in volume leads to a decrease in the concentration of fluorine, while a decrease in volume leads to dilution of the sulfuric acid by the fluoride solution. An increase in the diameter of the tube decreases the surface of the glass to be wetted and at the same time decreases the number of hydrophobic parts. The change in the surface of the glass etched with dilute HF solution, which was observed under the electron microscope, may be the result of an increase in the volume of the products formed during the surface chemical reaction.

SUMMARY

A study has been made of the possibility of detecting fluorine in small amounts of organic materials of different types, from nonwettability of glass, by using the technique employed for inorganic fluorides. It has been established that a chromic mixture does not break the bond C−F well enough. Fluorine cannot be detected in CF_3COOH and in fluorochlorides by this method. When this mineralization method is used, fluorine can only be detected in readily mineralized fluorides. 10-20 μg of fluorine can be detected in a drop in the case of fluoroanhydrides and in organic materials containing the group CFH_2.

The method has been improved by using a solution of $KMnO_4$ in oleum for mineralizing the organic compounds. The sensitivity of detection was thereby increased. In this case fluorine can be detected even in fluorochlorides and in compounds containing the CF_3 group. It is possible to detect from 1 μg F in a drop (for readily mineralized materials) to 10 μg F in a drop of a material which is difficult to mineralize (containing the group CF_3).

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QUANTITATIVE DETERMINATION OF CONDENSED AROMATIC HYDROCARBONS IN KEROSENE-GAS OIL FRACTIONS FROM DOLINSKAYA AND BITOVSKAYA PETROLEUMS BY THEIR ABSORPTION SPECTRA IN THE NEAR ULTRAVIOLET

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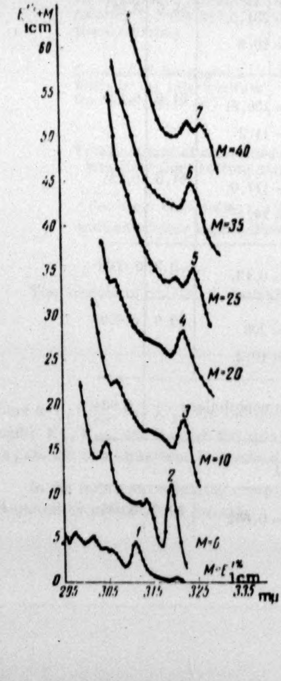
Quantitative determination of napthalene-type hydrocarbons in petroleum fractions has either not been carried out at all, or has only been carried out very approximately [1-4]. In the work described here we tried to determine the content of condensed aromatic hydrocarbons in kerosene-gas oil fractions from Dolinskaya and Bitovskaya petroleum by means of a combined method which we have developed.



Using chromatographic adsorption on silica gel (ASM) and fractional distillation (35 theoretical plates), we obtained 2-3 degree fractions containing mainly condensed aromatic hydrocarbons, from petroleum fractions taken under vacuum (200-375° in the case of Dolinskaya and 200-400° in the case of Bitovskaya petroleum).

The narrow fractions were examined spectrophotometrically on a SF-4 apparatus (Fig.). The ultraviolet spectra showed that the kerosene-gas oil fractions from Dolinskaya and Bitovskaya petroleum contains naphthalene, α- and β-methylnaphthalene, dialkylnaphthalenes – mainly 1,2-, 1,3-, 1,5-, 1,6-, and 1,7-isomers, trialkylnaphthalenes – mainly 1,2,7-, 1,3,6-, 1,3,5-, 1,2,5-, 1,4,6-, 1,2,8-, 1,3,7-, and 1,4,5-(in the Bitovskaya petroleum) and 1,2,5-, 1,2,7-, 1,3,6-, 1,4,6-, and 1,3,5-isomers (in the Dolinskaya petroleum). In addition to the compounds indicated, Dolinskaya petroleum was also shown to contain phenanthrene and 2,3-dialkylphenanthrene, while Bitovskaya petroleum contain anthracene homologs.

The narrow fractions which were similar in composition (on the basis of spectrophotometry) were combined and subjected to quantitative analysis. The results of the photometric measurements in the ultraviolet, and the calculated amounts of condensed aromatic hydrocarbons are given in the Table.

The amount of naphthalene, phenanthrene, 2,3-dialkylphenanthrenes, and homologs was calculated by means of the formula: $\frac{K'_\lambda}{K_\lambda} \cdot 100$ = wt. % of hydrocarbon in the fraction.

Quantitative Determination of Condensed Aromatic Hydrocarbons in Kerosene-Gas Oil Fractions from Bitovskaya and Dolinskaya Petroleum, from their Ultraviolet Absorption Spectra

Hydrocarbons found in the petroleum		Boiling range of the fraction, °C (760 mm)	Specific absorption coefficients of pure hydrocarbons calc. from the atlas [5,6]; K_λ for individual hydrocarbons; K_{mean} for groups of hydrocarbons (λ in mμ)	K'_λ specific absorption coefficients of kerosene-gas oil fractions containing condensed aromatic hydrocarbons	Hydrocarbon content, wt% in the fraction	Hydrocarbon content, wt% in the petroleum
Bitovskaya petroleum (up to 400° C)						
Naphthalene		200—218	$K_{221} = 983$; $K_{236} = 8,76$; $K_{311} = 2,03$	$K'_{221} = 125$; $K'_{236} = 1,2$ $K'_{311} = 0,237$	11,8	0,017
α-Methylnaphthalene		222—251	$K_{314} = 2,32$; $K_{319} = 0,528$	$K'_{314} = 0,604$ $K'_{319} = 0,764$	16,5	0,046
β-Methylnaphthalene			$K_{314} = 1,232$; $K_{319} = 3,802$		17,9	0,050
Dialkylnaphthalenes (possible isomers: 1,2- 1,3-, 1,5-, 1,6-, and 1,7-)		254—295	$K_{mean\,227} = 748$; $K_{mean\,247} = 7,5$	$K'_{227} = 368$; $K'_{244} = 12,4$	48,0	0,208
Trialkylnaphthalenes*	**Mainly: 1,2,7- 1,3,5-, and 1,3,6**	302—310	$K_{mean\,231} = 408$; $K_{mean\,244} = 10,3$	$K'_{231} = 231,5$, $K'_{247} = 10,8$	55,0	0,081
	Mainly: 1,2,5- and 1,4,6-	310—321	$K_{mean\,231} = 408$; $K_{mean\,247} = 10,3$	$K'_{231} = 256,6$; $K'_{247} = 11,3$	61,0	0,229
	Mainly: 1,2,5- 1,2,8-, 1,3,7- and 1,4,5)	326—350	$K_{mean\,231} = 408$; $K_{mean\,247} = 10,3$	$K'_{231} — 177,0$; $K'_{247} = 14,1$	41,0	0,224
Anthracene homologs		360 - 400	$K_{mean\,376-390} \sim 41,3$	$K'_{379} = 0,13$	~0,31	0,0005
Content of the naphthalenes in the intermediate fractions (up to 350°)		200—350	$K_{mean\,228} =$ 5[illegible]; $K_{mean\,245} = 9,2$	$K'_{228} = 208$, $K'_{245} = 10,2$	40,0	0,079
Total content of condensed aromatic hydrocarbons (apart from naphthalene homologs boiling above 350°)						0.934
Dolinskaya Petroleum (up to 375°)						
Naphthalene		200—226	$K_{311} = 2,03$	$K'_{311} = 0,682$	33,6	0,041

(continued)

Hydrocarbons found in the petroleum	Boiling range of the fraction, °C (760 mm)	Specific absorption coefficients of pure hydrocarbons calc. from the atlas [5,6]; K_λ for individual hydrocarbons; K_{mean} for groups of hydrocarbons (λ in mμ)	K'_λ specific absorption coefficients of kerosene gas oil fractions containing condensed aromatic hydrocarbons	Hydrocarbon content, wt %	
				in the fraction	in the petroleum
α-Methylnaphthalene	230—255	$K_{314} = 2,323$; $K_{319} = 0,528$	$K'_{314} = 0,915$; $K'_{319} = 1,166$	25,1	0,076
β-Methylnaphthalene		$K_{314} = 1,232$; $K_{319} = 3,802$		27,2	0,082
Dialkylnapthalenes (possible isomers: 1,2-, 1,3-, 1,5-, 1,6-, and 1,7-)	260—282	$K_{\text{mean}\,337} = 748$; $K_{\text{mean}\,347} = 7,5$	$K'_{337} = 350$; $K'_{344} = 10,0$	47,0	0,252
Trialkylnaphthalenes, mainly 1,3,5-*	282—296	$K_{\text{mean}\,331} = 408$; $K_{\text{mean}\,347} = 10,3$	$K'_{331} = 284$; $K'_{347} = 14,0$	68,0	0,133
Trialkylnaphthalenes, mainly 1,2,5- and 1,4,6-*	293—338	$K_{\text{mean}\,331} = 408$; $K_{\text{mean}\,347} = 10,3$	$K'_{331} = 282$; $K'_{347} = 13,3$	67,6	0,481
Phenanthrene	338—354	$K_{346} = 1,26$	$K'_{346} = 0,174$	~13,8	~0,008
Pheneanthrene homologs (mainly 2,3-dialkylphenanthrene)	354—375	$K_{340} = 0,825$	$K'_{340} = 0,26$	~31,5	0,014
Content of the naphthalenes in the intermediate fractions (up to 340°)	200—340	$K_{\text{mean}\,338} = 503$; $K_{\text{mean}\,348} = 9,2$	$K'_{338} = 253$; $K'_{348} = 12,0$	40,0	0,008
Total content of condensed aromatic hydrocarbons (apart from naphthalene homologs boiling above 340°)					1,185

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* Fractions containing trialkylnaphthalenes may possibly contain 1,2,3,4- and 2,3,6,7-tetrasubstituted naphthalene.

The amount of α- and β-methylnaphthalenes was calculated by solving the system of two linear equations:

$$K'_{314} = K_{314(\alpha)} \cdot C_\alpha + K_{314(\beta)} \cdot C_{(\beta)};$$

$$K'_{319} = K_{319(\alpha)} \cdot C_{(\alpha)} + K_{319(\beta)} \cdot C_{(\beta)},$$

Where K'_λ, K'_{314}, and K'_{319} are the specific absorption coefficients of the combined fractions at the given wavelength; K_λ, K_{314}, and K_{319} are the specific absorption coefficients of the pure, individual hydrocarbons; $C_{(\alpha)}$ and $C_{(\beta)}$ are the concentrations determined for α- and β-methylnapthalene (g/liter).

In the fractions containing complex mixtures of naphthalene hydrocarbons, the amount of the latter was calculated by means of the formula:

$$\frac{K'_{338} - K'_{348}}{K_{m338} - K_{m348}} \cdot 100 - \text{wt.\%}$$

The possibility of using this formula for group determination of naphthalene hydrocarbons has been demonstrated by Zimina and Siryuk [7].

In contrast to the authors mentioned, we calculated the mean absorption coefficients in the region 225-245 mμ, not for all the possible naphthalene hydrocarbons, but only for those which are present in the fractions as their main component. This appreciably increased the precision of the method, since the mean specific absorption coefficients ($K_{\text{mean } 225}$) calculated from the atlases [5, 6] for the di- and trialkylnaphthalenes differ by approximately 45%.

The precision of the method suggested can be evaluated by taking into account the following possible errors.

As a result of unavoidable losses during chromatographic separation and fractional distillation, the weight of the combined fractions is determined with a precision of up to 2-3% (taking into account the corresponding corrections for loss).

The condensed aromatic hydrocarbons are not completely separated from benzene homologs by the chromatographic technique, as a result of which the amount of di- and trialkylnaphthalenes found spectrophotometrically at 225-245 mμ, apparently exceeds the true content of such hydrocarbons in the fractions. Thus, the amount of naphthalene in the naphthalene fractions as found by means of K_{221} and K_{236} is 1% higher than the amount found in the same fractions using K_{311}. The difference in α- and β-methylnaphthalenes determined by means of K_{225}, K_{243}, and $K_{314-319}$ amounts to 5%.

The published values of the absorption coefficients of pure hydrocarbons, as we found in the case of naphthalene and α- and β-methylnaphthalenes, may differ by 3-5% from the corresponding values determined experimentally under our conditions.

The total relative error for the determination of naphthalene hydrocarbons in kerosene-gas oil fractions of Bitovskaya and Dolinskaya petroleum amounts to ±10%, as long as the small content of the components in the intermediate fractions, analyzed separately, is not taken into account.

The ultraviolet absorption method has a clear-cut advantage over other methods for the quantitative determination of condensed aromatic hydrocarbons in petroleum. For example, evaluation of the content of such hydrcarbons in petroleum by means of chromatography alone is too coarse (Table). The picric acid method, which has completely justified itself for the analysis of condensed aromatic hydrocarbons, is less accurate than the ultraviolet absorption method and requires a considerably longer time. In some cases, presumably, it would be useful to combine these techniques.

SUMMARY

A combined method has been developed for the determination of the content of condensed aromatic hydrocarbons in kerosene-gas oil fractions from Dolinskaya and Bitovskaya petroleums.

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.– Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

BUTYLRHODAMINE–A NEW REAGENT FOR PHOTOMETRIC DETERMINATION, EXTRACTION, PRECIPITATION, AND COPRECIPITATION OF ELEMENTS

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Many elements which can form complex hydrophobic anions such as $Zn(SCN)_4^{2-}$, $SbCl_6^-$, $HgBr_4^{2-}$ and similar anions, give so-called "colored solid phase reactions" [1]. Salts of heavy colored organic cations serve as reagents. As a result of these reactions colored precipitates of sparingly soluble salts appear, which are formed by the cation of the reagent and the complex anion of the element. These sparingly soluble salts can often be extracted by organic solvents [2, 3]; this fact is made use of for the extraction or the extraction-photometric determination of the elements. Finally, in the form of these compounds, the elements can be coprecipitated with organic coprecipitants [4-6]. Thus the reagents adopted are used for the photometric determination, precipitation, coprecipitation, and extraction of the elements.

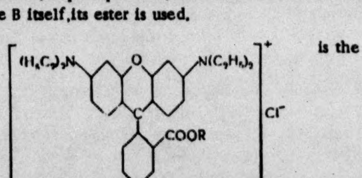
Many reagents have been recommended for this purpose, they include: methyl violet, crystal violet, rhodamine B, p-dimethylaminobenzene, anthrazo and a number of others [7-10]. These reagents are not universal. The action of each is limited more or less to a narrow pH range, and sometimes even the field in which they are applied is limited. When a given reagent is suitable for color solid phase reactions or coprecipitation it is not always suitable for extraction, etc.

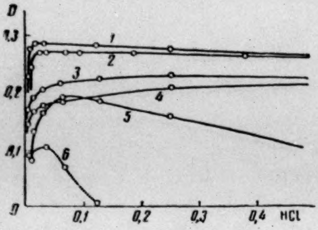
The greatest difficulties arise in connection with the small operating pH range. Thus, at acidities greater than 0.1-0.4 N, methyl violet is no longer suitable. In strongly acid solutions p-aminoazobenzene is suitable, but at pH> 4 its salts hydrolyze.

The best reagent which is suitable for a wide pH range is rhodamine B, which was first used by Eegriwe [11] for color reactions; other research workers followed him [8].

The authors of the present article have observed that the range of suitable pH values, and, particularly, completeness of precipitation, coprecipitation, and extraction of the elements can be considerably increased when, instead of rhodamine B itself, its ester is used.

Rhodamine B [1] is the salt of an organic cation containing





Effect of acidity on the sensitivity of colored solid phase reactions of rhodamine B esters. Concentrations: Tl) 0.8 μg/ml (5 μg/ml for methyl violet); reagent) $2 \cdot 10^{-5}$ M ($5 \cdot 10^{-5}$ M for methyl violet). 20 ml cuvette, green filter. 1) Isoamylrhodamine + $TlCl_4^-$; 2) butylrhodamine + $TlCl_4^-$; 3) benzylrhodamine + + $TlCl_4^-$; 4) octylrhodamine + $TlCl_4^-$; 5) rhodamine 3 B + $TlCl_4^-$; 6) methyl violet + $TlCl_4^-$.

a carboxyl group. The latter to some extent weakens the basic properties of the whole cation, and increases the solubility of the salts formed by rhodamine B, even in acid media. This unfavorable effect of the carboxyl group can be eliminated by esterifying it. When rhodamine B is esterified with not too light an alkyl radical, then it is possible, at the same time, to depress the solubility of the salts formed even further in line with the so-called "weighting" effect. The latter could be achieved by introducing heavy hydrophobic substituents into some other places in the rhodamine B molecule as well, e.g., substituting the C_2H_5 on the nitrogen atom by heavier alkyl radicals. Such substitutions, however, weaken the basic properties of the cation, apart from difficulties connected with the synthesis of such reagents. The introduction of heavy substituents into the aromatic nucleus complicates the synthesis to a very marked extent. Thus, alkylation of the carboxyl group would appear to be the only practical way of improving rhodamine B.

The ethyl ester of rhodamine B which is used as a dye under the name rhodamine 3B is a more valuable reagent than rhodamine B. It is natural to expect that other esters of rhodamine B may have equal or even better properties. In order to find out which of the possible esters have the most valuable properties as a reagent, we have synthesized and examined a number of esters of rhodamine B, they include: the n-butyl, isoamyl, n-octyl, and benzyl esters of rhodamine B.

With respect to the operating pH range within which colored solid phase reactions can be carried out, all these esters are superior to rhodamine B and are of equal value among each other. In order to compare the reagents according to this index, a study was made of the effect of the acidity on the sensitivity of colored solid phase reactions.

The anion $TlCl_4^-$ was used as test object, while for all the reagents tested, apart from methyl violet, which was taken as a reference, the conditions used were the same. The thallium concentration was 0.8 μg/ml while the concentration of the reagents was $2 \cdot 10^{-5}$ M. In the case of methyl violet, the thallium concentration was 5 μg/ml, while the methyl violet concentration was $2 \cdot 10^{-5}$ M. Into a 25 ml standard flask was introduced a solution of $Tl_2(SO_4)_3$ in 0.1 N HCl and the requisite amount of hydrochloric acid, 10-15 ml of distilled water was added, and the whole thoroughly mixed; 1.0 ml of the reagent was then added gradually and the solution finally made up to the mark with water. Five minutes after mixing, the light absorption of the solution obtained was measured in a 20 ml cuvette on a FÉK-N-54 photoelectrocolorimeter fitted with a green No. 5 filter (maximum transmission at 536 mμ), relative to a solution of the reagent of the same concentration. The results obtained are shown in the Fig., which also includes results for methyl violet for comparison.

In order to compare the reagents with respect to their suitability for extraction, the partition coefficients were determined during the extraction of thallium from solutions with varying acidities. Thallium was extracted in the form of the salt formed between the anion $TlCl_4^-$ and the cation of the rhodamine B ester, with an equal volume of toluene. The concentrations of thallium and of the reagents were the same as those used in the experiments on the effect of acidity on the sensitivity of the colored solid phase reactions.

Into a test tube with a ground-glass stopper was introduced the requisite amount of hydrochloric acid, and water was added so that the final volume was 2 ml; $Tl(NO_3)_2$ solution labelled with Tl^{204} was added in an amount such that the count rate was about 15,000 cpm, this was followed by the reagent and the whole thoroughly mixed, 2.0 ml of toluene was added and the mixture shaken vigorously for 3 min. After the mixture had separated out into layers, aliquots were taken from the upper and lower layers, and placed in 20 mm tall porcelain crucibles with an upper diameter of 23 mm; they were evaporated on a water bath and the activity determined on a torsion β-counter. The partition coefficients determined, which are ratios of the thallium concentration in the

TABLE 1

Effect of Acidity on the Extraction of Thallium. Concentrations: Tl) 0.8 μg/ml (5 μg/ml for methyl violet). Reagent: $2 \cdot 10^{-5}$ M

Reagent	HCl concentration, M	Partition coefficient	Reagent	HCl concentration, M	Partition coefficient
Methyl violet	0,5	0,82	Benzylrhodamine	0,5	7,1
	1,0	0,10		1,0	7,8
	2,0	0,004		2,0	16,7
Rhodamine B	0,5	3,7	Octylrhodamine	0,5	11
	1,0	1,4		1,0	13
	2,0	1,2		2,0	18
Astrafloxine	0,5	5,8	Isoamylrhodamine	0,5	7,9
	1,0	4,2		1,0	17
	2,0	4,2		2,0	28
Rhodamine 3B	0,5	5,4	Butylrhodamine	0,5	4,2
	1,0	4,3		1,0	11
	2,0	3,0		2,0	26

organic solvent layer to its concentration in the aqueous layer, are given in Table 1. Each value is the mean of 2-3 determinations.

The isoamyl and butyl esters of rhodamine B have been used for the coprecipitation of quadrivalent plutonium [12, 13]. The results of the coprecipitation given in Table 2 are taken from this work.

DISCUSSION OF RESULTS

A comparison of the results obtained for esters of rhodamine B as reagents, as a function of the dimensions of the alkyl radical, shows that the highest extraction and coprecipitation, and the highest sensitivity of the colored solid phase reactions, are achieved in practice when a C_4 alkyl is used.

Bearing in mind the difficulty of synthesizing esters with heavier alkyls, the most valuable representative of this group with respect to the sum total of the indices is the butyl ester which we propose to call "butylrhodamine."

The reagent butylrhodamine can be recommended for colored solid phase reactions, precipitation, coprecipitation, and extraction of elements which are capable of forming complex, not-too-hydrophilic anions.

Synthesis of Rhodamine B Esters

In developing methods for preparing rhodamine B derivatives, the method used for preparing rhodamine 3B from rhodamine B and ethyl chloride [14] was used as a basis, the only difference being that the alkyl bromide was used instead of the alkyl chloride. The alkyl bromides were obtained by the use of hydrobromic and sulfuric acids [15].

The butyl ester of rhodamine B. Fifty g of commercial rhodamine B hydrochloride is dissolved in 200 ml of water on heating on a boiling water bath. The dark-rose, hot solution is filtered in order to remove accidental contamination, and to the filtered solution is slowly added with stirring a solution of 25 g of NaOH in 100 ml of water. The sodium salt of rhodamine B which is precipitated is filtered off from the hot (!) solution on a Buchner funnel and dried in air.

Thirty g of the completely dry sodium salt of rhodamine B is placed in a round-bottom flask, and 54 ml of n-butyl bromide and 200 ml of butanol added; the mixture is heated under reflux on an oil bath for 10-12 hr, (the temperature of the oil bath is 120°). After cooling, the reaction mass is transferred to a porcelain basin and excess n-butyl bromide and butanol removed by evaporation on a water bath.

a) Butylrhodamine hydrochloride. The product remaining after evaporating off the butyl bromide and butanol is dissolved in hot water, and the still-hot solution acidified with concentrated hydrochloric acid until the solution gives an acid reaction to congo red. The butylrhodamine hydrochloride which separates out in a sirupy form on cooling is removed from the mother liquor by decantation and is dried at 35-40°.

TABLE 2

Coprecipitation of Pu^{IV} by the "Nitrate Mechanism." Volume of the Original Solutions 100 ml. Plutonium Dilution $1:1 \cdot 10^9$ (0.1 μg Pu in 100 ml). In Each Experiment 200 mg of the Test Coprecipitant was Added in the Form of Its 1% Solution

Coprecipitant	Concentration		Coprecipitation
	NH_4NO_3, %	HNO_3, M	Pu, %
Methyl violet chloride	30	0.6	4
	50	0.6	8
Nitron, acetate	30	0.6	8
	50	0.6	13
Diphenylguanidine, acetate	30	0.6	14
	50	0.6	18
Rhodamine B, chloride	30	0.6	21
	50	0.6	64.66
	50	1.8	74.75
Diantipyrylphenylmethane, hydrochloride	30	0.6	20
	50	0.6	30
	50	1.8	43.48
n-Phenylene-bis-(diantipyrylmethane)-hydrochloride	30	0.6	40
	50	0.6	60
	50	1.8	90.92
Amyl ester of rhodamine B, chloride	30	0.6	38
	50	0.6	80
	50	1.8	90.95
Butyl ester of rhodamine B (butylrhodamine, rhodamine 5B) chloride	30	0.6	30
	50	0.6	92.95
	50	1.8	99.100
			101

b) Butylrhodamine nitrate. The product remaining after evaporating off the butyl bromide and butanol is dissolved in hot water, the solution is cooled and acidified with concentrated nitric acid until an acid reaction to congo red is given; the solution is then neutralized with ammonia. The sirupy butylrhodamine nitrate which separates out is removed from the mother liquor by decantation and is dried at 35-40°.

The hydrochloride and nitrate salts of butylrhodamine are dark raspberry-red crystals, which are soluble in water, alcohol, and acetone; they are insoluble in benzene and toluene. They are not extracted from aqueous solutions by benzene, toluene, and chloroform.

1.87 g of the hydrochloride and 1.37 g of the nitrate salt dissolve in 100 ml of water at 20°.

Aqueous solutions of the hydrochloride and nitrate salts of butylrhodamine have an intensely rose color; when colored solid phase reactions are carried out, blue colors develop. The color does not change appreciably on acidifying to 0.1 N HCl.

Free chlorine decolorizes the solution, free bromine changes the color to a turbid orange; H_2O_2, $SnCl_2$, and $TiCl_3$ have no effect.

SUMMARY

Butylrhodamine (the butyl ester of rhodamine B) is recommended as a reagent for carrying out colored solid phase reactions and precipitation, for coprecipitation and extraction of elements which are capable of forming hydrophobic complex anions in acid media. Butylrhodamine is suitable for work in a wider acidity range than, for example, methyl violet or rhodamine B.

The sparingly soluble blue salts which are formed between butylrhodamine and the complex anions of elements can be extracted with C_6H_6, $CHCl_3$, etc; the extracts are rose colored.

The synthesis of butylrhodamine is described; it is prepared by the action of butyl bromide on the anhydrous sodium salt of rhodamine B.

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* Original Russian pagination. See C. B. Translation.

A STUDY OF THE SOLUBILITY OF ZIRCONIUM, THORIUM, AND URANIUM PHENYLARSONATES

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Precipitation of zirconium by means of phenylarsonic acid is carried out from strongly acid solutions [1, 2] while thorium is precipitated from acetic acid solutions [1, 3]. As far as we know, no quantitative studies have been made of the solubility of zirconium and thorium phenylarsonates. Usually, zirconium is precipitated in the form of a basic phenylarsonate [2]. The reaction leading to the formation of uranium phenylarsonates and the properties of the latter have not been studied in practice. There are indications that under the conditions used for the precipitation of zirconium and other quadrivalent metals, sexivalent uranium is not precipitated [3-5]. The pH at the beginning of the precipitation of uranyl by phenylarsonic acid has been established as 1.5, however, no indications were given of the concentrations used [6]. It is recommended that uranium be precipitated at pH 1-3 [3].

Reagents and experimental technique. Nitric acid solutions of zirconium nitrate marked with Zr^{95}, and of thorium nitrate marked with Th^{229} were used in the work. The solution of zirconium nitrate was heated beforehand in concentrated nitric acid for 30 min at 100° in order to convert zirconium into the nonhydrolyzed form. The preparation of Zr^{95} was used not more than 5 hours after its purification from the daughter element Nb^{95}. The nitric acid solutions of uranyl nitrate marked with U^{233} had a specific activity of 5000 disintegrations/ / min/mg. The latter was used in the course of not more than 30 days after extraction purification from the daughter radioactive elements. Quadrivalent uranium was obtained in acid solution by addition of five times its amount of rongalite [7].

The phenylarsonic acid preparation, "pure" grade, contained not less than 95% of the main component. The absence of arsenite in the preparation was established by a qualitative reaction in a carbonate medium with starch and iodine.

The solubility of the metal phenylarsonates was determined mainly by a precipitation technique, when the equilibrium solubilities are reached from saturated solutions in the presence of a precipitate [8, 9]. After mixing all the requisite reagents, the solutions were heated at 70-90° for about 15 min in order to make the precipitate coarser; the solutions together with the flock-like precipitates which separated out were then cooled for about an hour at 18 ± 3°. In certain, special cases, the solubility was also determined by the method of dissolving the precipitates obtained earlier. The precipitates were mixed in the solutions for 4-6 hours. In these cases the precipitates used were those that had been precipitated and made coarser by heating, i.e., precipitates having approximately the same structure as the precipitate used in the first technique.

The precipitates were removed by centrifugation, and the concentrations of zirconium, thorium, and uranium were determined radiometrically in the centrifugate. The uranium concentration was also determined by a luminescence method.

Solubility of uranium phenylarsonates. The phenylarsonates of quadrivalent and sexivalent uranium are pale-green in color.

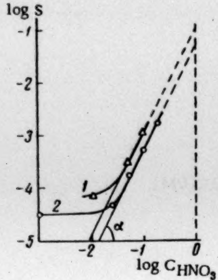

Fig. 1.

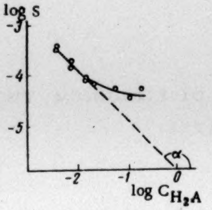

Fig. 2.

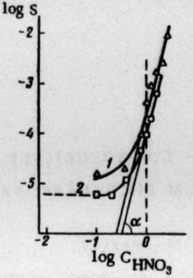

Fig. 3.

Fig. 1. Effect of acidity on the solubility of uranium (VI) phenylarsonate at a phenylarsonic acid concentration of 0.08 M. 1) Ammonium nitrate was not added; 2) ammonium nitrate 2 M.

Fig. 2. Effect of phenylarsonic acid concentration on the solubility of uranium (VI) phenylarsonate at a nitric acid concentration of 0.02 M.

Fig. 3. Effect of acidity on the solubility of uranium (IV) phenylarsonate at a phenylarsonic acid concentration of 0.04 M. 1) Ammonium nitrate was added until a concentration of 2 M with respect to the NO_3^- ion was reached; 2) ammonium nitrate was not added.

In the experiments on the determination of the solubility of the phenylarsonate of sexivalent uranium, the original concentration of the uranium was $2 \cdot 10^{-3}$ M. The effect of the acidity of the medium and the phenylarsonic acid concentration on the solubility is shown within logarithmic coordinates in Figs. 1 and 2. The effect of these factors on the solubility of the phenylarsonate of quadrivalent uranium is shown in Figs. 3 and 4. In the latter experiments the original uranium concentration was 10^{-3} M; only in experiments in which the nitric acid concentration was higher than 1 M was the uranium concentration 10^{-2} M.

On the solubility curves there is a point where there is a fairly sharp change from the inclined straight-line sections, coinciding with the tangents, to almost horizontal sections of the curves. The lowest values of the solubilities observed in the given experiments were those for the phenylarsonate of sexivalent uranium which was $3 \cdot 10^{-5}$ M and for the phenylarsonate of quadrivalent uranium which was about $1 \cdot 10^{-5}$ M. It is obvious that these values of the solubilities of the compounds will determine the loss of uranium in filtrates, in the case of analytical and other applications of reactions involving the precipitation of these compounds. Presumably, these values are those of the solubility of the nondissociated molecular forms of the compounds in water.

The curves obtained enable one to establish the following conditions for the most complete precipitation of uranium in the form of its phenylarsonates: for sexivalent uranium, at a phenylarsonic concentration of 0.08 M, the acidity of the solution should not exceed 0.01 M, while for quadrivalent uranium at a reagent concentration of not less than 0.04 M, the acidity should be higher than 0.3 M.

On the inclined sections of the solubility curves, it is obvious that in the case of sexivalent uranium the solubility depends on the second power of the hydrogen ion concentration of the solution (the tangent of the angle made by the straight line in Fig. 1 with the horizontal is approximately 2), and on the first power of the phenylarsonic acid concentration (tangent α in Fig. 2 is approximately 1). While in the case of quadrivalent uranium the solubility depends on the fourth power of the hydrogen ion concentration (Fig. 3) and on the second power of the phenylarsonic acid concentration (Fig. 4).

It follows from this that precipitation of uranium ions proceeds according to the following schemes:

$$UO_2^{2+} + H_2A \rightleftarrows \downarrow UO_2A + 2H^+; \qquad U^{4+} + 2H_2A \rightleftarrows \downarrow UA_2 + 4H^+;$$

where H_2A is phenylarsonic acid.

The solubility of zirconium and thorium phenylarsonates. The effect of the acidity of the solution on the solubility of zirconium and thorium phenylarsonates for a constant concentration of the reagent is shown in Fig. 5. In Table 1 are shown some additional results on the solubility of zirconium phenylarsonate in water, in hydrochloric and sulfuric acid solutions, and on the effect of phenylarsonic acid on the solubility of thorium phenylarsonate. In addition, Table 1 also contains results obtained by the method of dissolving the precipitates formed beforehand. In experiments on precipitation, the original concentration of the zirconium or thorium was 10^{-3} M, apart from the last point on curve 1, Fig. 5 and experiment 7, Table 1, where the original concentration was 10^{-2} M.

Determination of the composition of zirconium phenylarsonate formed in 1 M nitric acid solutions under the conditions used in our work showed that: the precipitate, washed with water and dried at 200°, weighed 150.0 mg; on subsequent calcination at 1100°, 36.0 mg of zirconium dioxide was obtained, which corresponds to 27.0 mg or 18% of zirconium. The calculated zirconium content for the normal phenylarsonate is 18.7%.

Thorium phenylarsonate precipitated at pH 1 and dried at 200°, weighed 41.0 mg; on calcining at 1100°, 16.5 mg of thorium dioxide was obtained; this corresponds to 14.5 mg or 36.5% thorium. The calculated value for thorium in the normal phenylarsonate is 36.8%.

TABLE 1

Expt. No.	Compound	Acidity of the solution	Phenylarsonic acid, M	Solubility, $M \cdot 10^5$	K_r
1	Zirconium phenylarsonate	Water	—	0,2*	—
2	Ditto	0,2 *M* HNO_3	0,02	0,5*	—
3	» »	2,2 *M* HCl	0,01	0,8	—
4	» »	3,3 *M* HCl	0,01	0,8	—
5	» »	4,4 *M* HCl	0,01	0,8	—
6	» »	6,7 *M* HCl	0,008	14	11,3
7	» »	10 *M* HCl	0,003	900	11,1
8	» »	1 *M* H_2SO_4	0,022	0,2	—
9	» »	2 *M* H_2SO_4	0,022	1,7	—
10	» »	3,4 *M* H_2SO_4	0,022	37	~9
11	Thorium phenylarsonate	0,005 *M* HNO_3	0,02	1,1*	—
12	Ditto	0,3 *M* HNO_3	0,05	95	3,5
13	» »	0,3 *M* HNO_3	0,03	146	3,8
14	» »	0,3 *M* HNO_3	0,02	172	4,1

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* The solubility was determined by the method of dissolving the precipitate obtained beforehand.

It is clear from the solubility curves in Fig. 5, as in the case of uranium phenylarsonates, that there is a sharp change from the inclined, almost linear sections, to the horizontal sections of the curves. It was shown that the lowest solubility of zirconium phenylarsonate in acid solutions, as determined by different methods – precipitation and dissolution – almost coincides with its solubility in water (compare experiments 1-5 and 8 in Table 1 and curve 2, Fig. 5).

The solubility curves shown, and the results given in Table 1, allow one to establish conditions for ensuring most complete precipitation when phenylarsonic acid is used as precipitant: for zirconium at a reagent concentration of 0.005 M, the acidity of the solution should not be less than 2 M, while for thorium at a reagent concentration of 0.08 M, the acidity of the solution should not be higher than 0.03 M. In the case of zirconium, the acidity can be increased to 4 M and higher as long as the phenylarsonic acid concentration exceeds 0.01 M. While if zirconium is precipitated in a sulfuric acid medium, then the acidity of the solution should not exceed 2 M even when the reagent concentration is 0.02 M.

As is evident from Fig. 5, the tangent of the angle made by the tangents to the solubility curves of zirconium and thorium phenylarsonsates (tangent α) is equal to 4, i.e., their solubility depends on the fourth power of the hydrogen ion concentration. The results given above on the determination of the composition of the compounds confirms that formation of the normal phenylarsonates occurs. Accordingly, precipitation of Zr^{IV} and Th^{4+} proceeds according to the scheme:

$$M^{IV} + 2H_2A \rightleftarrows MA_2 + 4H^+;$$

where H_2A is phenylarsonic acid.

Calculation of the reaction constants. Since the tangents to the solubility curves can be interpreted by means of the schemes given above for the reactions, they can be used for calculating the constants of the precipitation reaction, because the formation constant of the insoluble phenylarsonates can be expressed as follows:

$$K_r = \frac{[H^+]^n}{[M^{n+}][H_2A]^{\frac{n}{2}}},$$

where K_r is the constant of the formation reaction, n is the charge on the cation; by taking logarithms and transforming this expression we obtain:

$$[M^{n+}] = \log S = \lg \frac{1}{K_r [H_2A]^{\frac{n}{2}}} + n \log [H^+],$$

for $[H_2A]$-const. (tangents to curves in Figs. 1, 3, and 5), and

$$\log [M^{n+}] = \log S = \log \frac{[H^+]^n}{K_r} - \frac{n}{2} \log [H_2A]$$

for $[H^+]$ approximately equal to $[HNO_3]$-const (tangents to the curves in Figs. 2 and 4). Here S is the analytically determined concentrations of the metals, which, as follows from Figs. 1-5, can be equated to the concentrations of M^{n+} cations, if the value of the solubility is equal to not less than $10^{-4} - 5 \cdot 10^{-5}$ M.

Taking into account the fact that the equations given above for the straight lines are the equations of the corresponding tangents, it is possible to determine their free terms from the value of the segment of the ordinate for zero values of the abscissa, and then calculate K_r.

Since it is difficult to calculate activity coefficients at high salt concentrations, the concentration constants of the reaction are given here. The corresponding ionic strength of the solutions was calculated by the normal method from the concentrations of the strong electrolytes present in solution: ammonium nitrate, nitric or hydrochloric acid. In a series of experiments in which the acidity was varied, an evaluation was made of the mean value of the ionic strength for points corresponding to the linearly sloping sections of the curve, i.e., for sections coinciding with the tangents; in these cases the ionic strength is indicated approximately.

Thus, the following values were found for uranium (VI) phenylarsonate: according to Fig. 1, $\log K_r = 2.0$ (ionic strength μ approximately 0.1) and $\log K_r = 2.4$ ($\mu = 2$), and according to Fig. 2, $\log K_r = 2.4$ ($\mu = 0.02$), mean $\log K_r = 2.2 \pm 0.2$; while for uranium (IV) phenylarsonate, according to Fig. 3, $\log K_r = 6.8$ (μ approximately 1) and $\log K_r = 6.5$ ($\mu = 2$), and according to Fig. 4, $\log K_r = 6.1$ ($\mu = 0.5$), mean $\log K_r = 6.5 \pm 0.3$. Since a linear relationship is not observed between $\log K_r$ and the ionic strength (μ), according to the results given above, the mean value of K_r is calculated. According to Fig. 5, for zirconium phenylarsonate $\log K_r = 11.8$ (μ approximately 5, nitric acid media), while for thorium phenylarsonate $\log K_r = 3.7$ (μ approximately 0.5).

According to the results of a series of experiments (Table 1) it is also possible to calculate $\log K_r$ for zirconium and thorium phenylarsonates. In this case use can only be made of those points for which, as noted above, the solubility exceeds 10^{-4} M, i.e., when the analytically determined concentration of the metal can be equated to the concentration of the cation. The average value of $\log K_r$ calculated in this way for zirconium phenylarsonate in hydrochloric acid solutions is $\log K_r = 11.2 \pm 0.1$. Since the difference for nitric and hydrochloric acid solutions is not great, it is possible to take the mean value $\log K_r = 11.5 \pm 0.3$ (μ from 4 to 10).

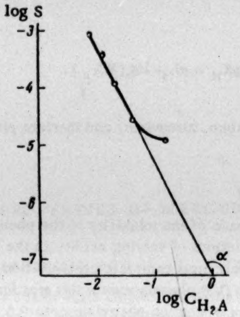

Fig. 4.

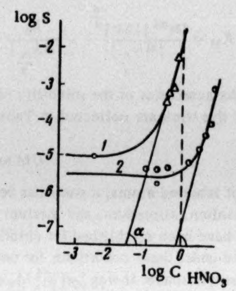

Fig. 5.

Fig. 4. Effect of phenylarsonic acid concentration on the solubility of uranium (IV) phenylarsonate at a nitric acid concentration of 0.5 M.

Fig. 5. Effect of the acidity of the solutions on the solubility of zirconium and thorium phenylarsonates. 1) Solubility curve of thorium phenylarsonate at a phenylarsonic acid concentration of 0.08 M; 2) solubility of zirconium phenylarsonate at a phenylarsonic acid concentration of 0.005 M.

TABLE 2

Compound	Lowest solubility, M	log K_r	pL_s	$pK_{Inst.}$
Uranium (VI) phenylarsonate	$3 \cdot 10^{-5}$	2,2±0,2	14	9,5
Uranium (IV) phenylarsonate	$1 \cdot 10^{-5}$	6,5±0,3	30,5	25,5
Zirconium phenylarsonate	$(0,5 \pm 0,2) \cdot 10^{-5}$	11,5±0,3	35,5	30
Thorium phenylarsonate	$1 \cdot 10^{-6}$	3,8±0,3	28	23

On the other hand, the formal constant of the reaction in sulfuric acid media, which can be calculated on the basis of the results of experiment 10, Table 1, differs very strongly: log K_r is about 9.

On the basis of the results of experiments 12-14, Table 1, it is possible to calculate K_r for the formation of thorium phenylarsonate, log $K_r = 3.8 \pm 0.3$ ($\mu = 0.3$). The agreement in K_r in both cases is good; mean log $K_r = 3.8 \pm 0.3$.

Following the generally accepted characteristic of sparingly soluble compounds, it is possible to calculate the solubility product L_s of phenylarsonates. Knowing the constant of the acid dissociation of phenylarsonic acid, which is given by $K_{diss} = 10^{-12}$ [10], we have:

$$L_s = [M^{n+}][A^{2-}]^{\frac{n}{2}} = K_{diss}^{\frac{n}{2}}/K_r \quad \text{or} \quad pL_s = \frac{n}{2}\, sK_{diss} + \log K_r.$$

Further, having assumed that the solubility of phenylarsonates under conditions where the most complete precipitation is observed is determined by the solubility of their undissociated forms $MA_{n/2}$, it is possible to calculate the instability constants of these compounds:

$$K_H = \frac{[M^{n+}][A^{2-}]^{\frac{n}{2}}}{[MA_{\frac{n}{2}}]} = \frac{L_s}{[MA_{\frac{n}{2}}]} \quad \text{or } pK_H = pL_s + \log[MA_{\frac{n}{2}}].$$

The quantitative characteristics of the solubility of uranium, zirconium, and thorium phenylarsonates determined in the course of this work are collected in Table 2.

SUMMARY

Using the method of labelled atoms, a study has been made of the solubility of the phenylarsonates of sexi- and quadrivalent uranium, zirconium, and thorium in solutions of varying acidity in the presence of phenylarsonic acid. Conditions have been established for ensuring their most complete precipitation, and their solubility has been determined under these conditions: for uranium (VI) phenylarsonate this was found to be $3 \cdot 10^{-5}$M, while for uranium (IV) phenylarsonate it was $1 \cdot 10^{-5}$ M, and for zirconium phenylarsonate $0.5 \pm 0.2 \cdot 10^{-5}$ M and for thorium phenylarsonate 10^{-5} M.

The logarithms of the concentration constants of the reactions leading to the formation of the phenylarsonates have been calculated; they were found to be 2.2 ± 0.2 for uranium (VI) phenylarsonate, 6.5 ± 0.3 for uranium (IV) phenylarsonate, 11.5 ± 0.3 for zirconium phenylarsonate, and 3.8 ± 0.3 for thorium phenylarsonate.

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THE REDUCING PROPERTIES OF MERCURY

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During studies of electrochemical processes which occur on mercury or amalgam electrodes, due attention is not usually given to the side reactions which accompany the main electrode process. In particular, little attention is given to the direct interaction of mercury with materials reduced on the cathode, and to its anodic oxidation together with the other metals present in the amalgam. Underestimation of side reactions may sometimes lead to a one-sided interpretation of the mechanism of the electrode processes. This interpretation has, in our opinion, been made in attempts to explain the steplike waves in works published on polarography by Shvaer and Sukhi on reduction of selenite and tellurite [1], by Issa on reduction of permanganate [2], and by others on reduction of multivalent ions [3, 4]. Formation of steplike waves is also observed during the reduction of ions having only one degree of oxidation. Their appearance in this case is explained by reduction [5, 6] of complexes with different instability complexes. However, the possibility is not excluded that formation of a complex wave is determined by the superposition of the anodic process of the oxidation of mercury on the cathodic process of the reduction of the ions. The appearance of sparingly soluble materials as the result of side reactions may complicate the polarograms even more [7].

During reduction of metals by amalgams, participation of mercury in the reduction reaction is usually not taken into account either.

The reducing property of mercury is determined by the chemical nature of the anions present in solution and adsorbed on its surface. This was pointed out as long ago as 60 years by Paschen [8].

The effect of anions on the potential of mercury can be seen from Table 1.

A comparison of these results with the values of the solubility products of the corresponding mercury salts, and also with the instability constants of the mercury complexes, graphically shows the connection between the depolarization potential of mercury by one ion or another and the solubility (or stability) of the compounds formed between mercury and the corresponding ion. The lower the solubility the greater the negative potential. The existence of such a relationship permits one to carry out quantitative polarographic determination of certain anions [9, 10].

The kinetics and the mechanism of the anodic oxidation of mercury has been studied to a comparatively small extent. Wakkad [11] has given an equation which expresses the relation between the rate at which mercury dissolves and the extent to which the electrode is polarized. All other values being constant, the equation given by Wakkad takes the form

$$V = \text{const} + \frac{RT}{\alpha ZF} \ln I,$$

where V is the difference between the electrode potential and the equilibrium potential; I is the current density; Z is the number of electrons; and F is the Faraday number.

TABLE 1

Normal Oxidation Potentials of Mercury (Normal Hydrogen Electrode) in Various Media

Electrode reaction	E_0, volt	Electrode reaction	E_0, volt
$Hg + H_2O - 2e \rightarrow HgO + 2H^+$	+0,926	$2Hg + 2CNS^- - 2e \rightarrow Hg_2(SCN)_2$	+0,22
$2Hg + SO_4^{2-} - 2e \rightarrow Hg_2SO_4$	+0,615	$2Hg + 2Br^- - 2e \rightarrow Hg_2Br_2$	+0,139
		$2Hg + H_2O - 2e \rightarrow Hg_2O + 2H^+$	+0,123
$2Hg + CrO_4^{2-} - 2e \rightarrow Hg_2CrO_4$	+0,41	$2Hg + 2I^- - 2e \rightarrow Hg_2I_2$	−0,041
$Hg + 2IO_3^- - 2e \rightarrow Hg + (IO_3)_2$	+0,40	$Hg + 4CN^- - 2e \rightarrow Hg(CN)_4^{2-}$	−0,37
$2Hg + CO_3^{2-} - 2e \rightarrow Hg_2CO_3$	+0,32	$Hg + S^{2-} - 2e \rightarrow HgS$	−0,70
$2Hg + 2Cl^- - 2e \rightarrow Hg_2Cl_2$	+0,268		

Thus, the relationship between the logarithm of the current strength and the potential, during anodic dissolution of mercury, is expressed by a straight line. However, according to this author, this relation is only preserved at very low current densities.

Cousens, Ives, and Pittman [12-14] have studied the mechanism of the anodic oxidation of mercury. They subjected a mercury electrode to polarization by an interrupted direct current of low value. In the breaks between the individual current impulses, micropolarization tests were carried out (forward and reverse) in order to determine the extent of the reversibility of the electrode. They found that a mercury electrode in a hydrochloric acid solution behaves itself irreversibly, even after passing a fairly large amount of electricity through it, when a precipitate of Hg_2Cl_2 is formed. The irreversibility was confirmed by the existence of a hysteresis loop between the ascending and descending branches of the polarization curve. But, after a long interval between such impulses, the electrode became reversible again. It was established that the changes which occur in the potential of the mercury electrode with changes in the amount of electricity passed through the solution are not linear; this follows from the fact that the curve passes through a maximum. The potential of the maximum is several millivolts more positive than the potential of the reversible calomel electrode. It was also found that in order to reach the potential of the calomel electrode, it is necessary to expend a considerably greater amount of electricity than the theoretical amount. Their research led the authors to the conclusion that the primary electrode reaction during anodic polarization of mercury in hydrochloric acid solutions (current density 0.25 $\mu a/cm^2$) is the formation of mercuric ions. Calomel is then formed as the result of a secondary reaction: $Hg^{2+} + Hg^0 \rightarrow Hg_2^{2+}$. At very low current densities generation of Hg_2^{2+} and Hg^{2+} in equilibrium concentration should also occur, since the electrode in this case deviates only insignificantly from the equilibrium state. Application of higher current densities does not alter the mechanism of the process. However, the rapid covering of the mercury surface by Hg_2Cl_2 leads to passivation of the electrode and to a discharge of chlorine ions. Subsequently, the liberated chlorine oxidizes the Hg_2Cl_2 and depassivizes the electrode.

The presence in solution of ions or molecules which are capable of being reduced on the dropping-mercury electrode may complicate or modify the over-all electrode process. It is known that the reduction potentials of many anions on the dropping-mercury electrode are shifted towards more negative values as compared with their potentials on solid electrodes, particularly platinum ones. This may be explained on the grounds that at those potentials at which anions are reduced on a platinum electrode, anodic oxidation of mercury occurs at the same time on a mercury electrode. As a result of the superposition of the latter process on the reduction of the anions, the cathodic wave may disappear completely, when the oxidation current of mercury exceeds the cathodic current for the reduction of the anions. In actual fact, in this case direct interaction of mercury with the reduced anions will occur. In all cases when the rate at which mercury is oxidized anodically is higher than the rate at which the anions are reduced, the cathodic wave for the reduction of the anions will be absent, and will only appear at those potentials at which the anodic oxidation of mercury ceases. The wave obtained at these potentials will correspond either to the direct reduction of the given ion, or the reduction of mercury ions formed as a result of the interaction of metallic mercury with reducing ions. Opinion on this point differs. Thus, Simpson and Evans [15] assume that in the anodic region metallic mercury in reducing ions of the noble metals gives an equivalent amount of mercury ions, e.g.:

$$2Au^{3+} + 6Hg \rightarrow 2Au^0 + 3Hg_2^{2+}$$

TABLE 2

Interaction of Mercury with Ions in Neutral and Alkaline Solutions*

Composition of the supporting electrolyte	MnO_4^-		CrO_4^{2-}		$S_2O_8^{2-}$		MoO_4^{2-}		Fe^{3+}		Cu^{2+}	
	reaction product	potential, volt	reaction product	potential, volt	reaction product	potential, volt	reaction product	potential, volt	reaction product	potential, volt	reaction product	potential, volt
NH_4Cl	MnO_2 Hg_2Cl_2	+0,64	The mercury forms a sludge	+0,33	SO_4^{2-} Hg_2Cl_2	+0,65	0	+0,34	Fe^{2+} Hg_2Cl_2	+0,35	0	+0,37
NH_4Cl NH_4OH	O	+0,41	The mercury forms a sludge	+0,30	SO_4^{2-} Hg_2O	+0,31	0	+0,35	—	—	0	+0,33
$(NH_4)_2SO_4$	MnO_2 Hg_2SO_4	+0,66	The mercury forms a sludge	+0,51	Hg_2SO_4	+0,68	0	+0,40	0	+0,40	0	+0,51
KSCN	—	—	0	+0,21	—	—	The solution becomes blue-green	+0,13	$Hg(SCN)_2$ Decolorized, no precipitate	+0,30	—	—
KI	—	—	0	−0,06	—	—	The solution becomes blue	−0,09	$Hg(I)_4^{2-}$ No precipitate	−0,03	—	—
NaOH	MnO_4^{2-} Hg_2O	+0,45	0	+0,15	SO_4^{2-} Hg_2O	+0,33	—	+0,12	—	—	—	—

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* Supporting electrolyte concentration 0.5 M, concentration of the various ions 0.05 M. (1) signifies that the reaction was not studied because of the interaction of the ions with the supporting electrolyte; (0) signifies absence of interaction between the ions and mercury.

TABLE 3

Interaction of Mercury with Certain Ions in Acid Solution

Ion	HCl 1–6 *N*		H_2SO_4 1–6 *N*	
	reaction products	reduction potential, volt	reaction products	reduction potential, volt
MnO_4^-	Mn^{2+}, Hg_2Cl_2 MnO_2	+0,22	Mn^{2+} Hg_2SO_4, MnO_2	+0,70
CrO_4^{2-}	Cr^{3+}, Hg_2Cl_2	+0,20	Cr^{3+}, Hg_2SO_4	+0,57
MoO_4^{2-}	Mo^V, Mo^{III}, Hg_2Cl_2	+0,16	Does not react	+0,37
VO_3^-	V^{4+}, Hg_2Cl_2	+0,30	» »	+0,42
SeO_3^{2-}	HgSe, sludge	+0,11	» »	+0,19
TeO_3^{2-}	HgTe*	+0,17	» »	+0,18
Fe^{3+}	Fe^{2+}, Hg_2Cl_2,sludge	+0,19	» »	+0,68
Cu^{2+}	Cu_2Cl_2, Hg_2Cl_2,sludge	+0,19	» »	+0,36
IO_3^-	Hg_2Cl_2, ClI	+0,21	» »	+0,31
$S_2O_8^{2-}$	Hg_2Cl_2, SO_4^{2-}	+0,27	Hg_2SO_4	+0,70

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* The reduction proceeds in concentrated hydrochloric acid solutions (> 4N).

while the cathodic wave corresponds to the reduction of mercury ions:

$$Hg_2^{2+} + 2e \longrightarrow 2Hg$$

Kivalo, Laitinen [16] and other authors [17] are of the same opinion. But in a number of cases [2-4, 18, 19] the cathodic waves are explained by the direct reduction of ions ($S_2O_8^{2-}$, MoO_4^{2-}, MnO_4^-, etc.) on the dropping-mercury electrode. A correct interpretation of the mechanism of electrode processes requires that the whole complex of reactions accompanying polarography should be taken into account. In a particular case, e.g., reduction of tellurium, it is necessary to take into account the depolarization of mercury by tellurite and telluride ions and the formation of precipitates between mercury and these ions.

Thus, a study of the interaction of mercury with a number of ions in the presence of various depolarizers is of undoubted interest. A solution of this question would enable one to give a more correct interpretation of the nature of the polarographic waves and to evaluate the extent to which mercury participates in the reduction of metal ions.

In the work described here, we studied the reduction of copper (II), iron (III), selenite, tellurite, permanganate, dichromate, molybdate, iodate, vanadate, persulfate, and arsenate ions by metallic mercury in various media.

Indications are given in the literature [20-25] on the interaction of mercury with a number of ions. Some of these reactions have been used during the titrimetric determination of oxygen-containing anions for their reduction. However, the reactions indicated have for the most part been carried out in hydrochloric acid solutions. In addition, reduction was effected without any measurements of the potential of mercury. Measurement of this potential during the reduction process is very important, since it permits one to explain the change in the reducing properties of mercury with changes in the experimental conditions.

The supporting electrolytes which we used were neutral, alkaline, and acid materials which shift the oxidation potential of mercury; they included: sulfuric and hydrochloric acids, the ammonium salts of these acids, an ammonia–ammonium chloride mixture, potassium thiocyanate, potassium iodide, and sodium hydroxide.

The reactions were studied by shaking a solution containing the test ions and the appropriate supporting electrolyte with mercury. Shaking was carried out either in a separating funnel or in a special 50 ml vessel provided with a mechanical stirrer and an attachment for measuring the potential of the mercury. After a 15-20 min shaking the mercury was removed from the solution, any precipitates which might have been formed being filtered off, and the precipitate and solution analyzed separately for their content of reaction products. The precipitates were also analyzed spectrographically. The experimental results are given in Tables 2 and 3.

As is evident from the results given in Table 2, in nonacidified solutions mercury can reduce permanganate, persulfate, and iron(III) ions, and, apparently, molybdate,[*] while reduction of iron ions only occurs in the presence of strong depolarizers (halide and thiocyanate ions). Iodide ions, as is known, are themselves capable of reducing iron, elemental iodine being formed. On shaking a mixture of iodide and iron (III) solutions with mercury, the iodine is decolorized and reduction of iron proceeds to completion.

TABLE 4

Cementation of Tellurium by a Cadmium Amalgam

HCl concentration M	Cd isolated in the solution, g	Te found in the precipitate, g	Yield of Te with respect to Cd, %
1	0,3850	0,3366	144,7
2	0,3853	0,3312	142,3
3	0,3805	0,3312	144,7
4	0,3870	0,3360	144,7
5	0,3800	0,3368	142,3

Note: Amount of tellurium taken for cementation 0.3310 g; amount of cadmium taken for cementation 0.410 g.

In contrast to other ions, permanganate ions are reduced by mercury even in strongly alkaline solutions. Ions such as selenite, tellurite, vanadate, iodate, copper (II), and arsenate do not interaction with mercury in any of the solutions indicated in Table 2. The behavior of mercury in each concrete case is in good agreement with the values of its potentials.

In acid solutions (Table 3) a number of additional ions are included in the reduction reaction: selenite, tellurite, chromate, iodate, vanadate, copper (II).

It should be noted that selenite, tellurite, vanadate, iodate, iron (III), copper (II) ions are only reduced in hydrochloric acid solutions, they are not reduced in sulfuric acid solutions. Here, presumably, the difference in the depolarizing effect of chloride and sulfate ions becomes apparent. Arsenate ions do not interact with mercury even in acid solutions.

The list of ions capable of being reduced by mercury, obviously, is not limited to the ions listed here. But even the small amount of experimental evidence given in Tables 1 and 2 is sufficient to indicate clearly the reactivity of mercury with respect to a whole series of ions. These results enable one to affirm that during polarography of the ions which we have studied, there will occur interaction between them and mercury with formation (in most cases) of sparingly soluble compounds. This interaction should lead to a drop in, and frequently even to complete disappearance of, the diffusion current of the materials being reduced. The true value of the reduction current is only attained at potentials at which oxidation of mercury ceases. In this connection, during the polarographic process one might expect the appearance of step-shaped waves even in the absence of a stepwise reduction of the materials being polarographed.

As an example of the participation of mercury in the reduction of metal ions by the amalgams of more-negative metals one can induce the reduction of copper by cadmium and amalgam.

In a previous study of this process, we established that copper is reduced by a cadmium amalgam (0.5% Cd) at a definite, almost constant, potential (− 0.4 volt) to the metal. After a certain time interval there is observed a potential jump to positive values. After the potential jump the reduction process continues, but in this case univalent copper and not copper metal is formed. It might be assumed that in the reduction of copper to the univalent state only cadmium participates. But the results of experiments on the reduction of copper by mercury (Table 3) showed that mercury is capable, at a given potential value, of reducing copper in hydrochloric acid solutions. Analysis of the solution and precipitate formed during the cementation of copper by the amalgam, showed that mercury and cadmium at a given positive potential can simultaneously participate in the reduction of copper.

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[*] On shaking a molybdate solution in a supporting electrolyte of KSCN and KI with mercury, the color of the solution changes to blue-green and blue, respectively. When no mercury is present this is not observed. We did not establish the extent of the reduction.

Simultaneous participation of mercury in the reduction reaction was also observed during the cementation of tellurium (IV) by a cadmium amalgam in hydrochloric acid solutions (Table 4). The yield of tellurium with respect to cadmium exceeded 100% as a result of its reduction not only by cadmium, but also by mercury. Under these conditions mercury reduced tellurium (IV) at negative potentials (−0.13 volt) (normal hydrogen electrode). As soon as all the cadmium had been removed from the amalgam, there was observed a steplike change in the potential of the amalgam to more positive values, but reduction of tellurium by mercury did not cease even at this positive potential value.

SUMMARY

A study has been made of the reduction of a number of ions by metallic mercury in various solutions containing ions which can shift the potentials of the anodic oxidation of mercury.

It has been shown that permanganate and persulfate ions are reduced by mercury in neutral, alkaline, and acid solutions; iron (III) and molybdate in nonacidified and acid solution. Selenite, tellurite, vanadate, iodate, chromate, copper (II) are only reduced in acid solutions, a very strong effect on the reduction being displayed not only by the acidity of the solution, but also by the presence of other anions which shift the potential of the anodic oxidation of mercury.

The mercury potentials during the reductions have been measured. The value of the mercury potential depends on both the nature of the depolarizer and on the nature of the ion being reduced.

It has been shown that during the cementation of copper and tellurium by a cadmium amalgam, mercury participates simultaneously with the cadmium in the reduction reaction.

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THE USE OF STATIONARY MERCURY ELECTRODES IN OSCILLOGRAPHIC POLAROGRAPHY

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Oscillographic polarography permits the use of stationary electrodes for analytical purposes because of the short time it takes to record the current–voltage curves [1-2]. In such cases the value of the current is established very rapidly and is well reproduced. Polarographic maxima do not appear on the current–voltage curves in most cases, and it is therefore unnecessary to add surface-active materials to the solution. Dissolved oxygen does not distort the current–voltage curves, and reproducible results are obtained without removing oxygen from the test solution [3].

Some research workers [2, 4] have used a mercury pool as a cathode for the determination of materials at concentrations less than 10^{-5} M by oscillographic polarography. The determination was carried out in the absence of dissolved oxygen. Electrolysis on stationary electrodes in the presence of dissolved oxygen is of essential importance for the automatic control of plant streams. In this connection a series of experiments was carried out on the quantitative determination of certain elements in the presence of O_2. All the measurements were made on a GEOKhI oscillographic polarograph [5]. The peak potential (φ_P) and the half-peak potential ($\varphi_{P/2}$) are given relative to the saturated calomel electrode.

Electrolysis of the Quiescent Liquid

The electrolytic cell (Fig. 1) which is an open glass cylinder (internal diameter 4.5 cm, height 2.5 cm) consisted of two stationary mercury electrodes. The polarizing electrode was mercury in a narrow tube with an internal diameter of 0.56 cm and 1.6 cm long, while the nonpolarized electrode was mercury in the wide part of the cylinder. The area of the mercury surface in the tube was approximately one fiftieth of the area of the mercury in the large cylinder. The inner glass cylinder was provided with four small holes for the inert gas to escape. The outer cylinder served as a water seal. In cases where oxygen was removed from the test solution, the cell was closed with a lid into which were fused a thin tube for passing through hydrogen, a calomel electrode, and a tube for an agar siphon. The calomel electrode was used for determining the potential of the polarizing mercury electrode.

The cell was mounted in a plastic beaker fitted with plugs. The plugs fitted into the socket of the setup connected to the apparatus by a coaxial wire.

In order to prevent the electrolyte from flowing between the mercury and the glass, the inner surface of the tube was covered with a thin film of silicone. The surface area of the mercury (S) was determined by means of a microscope and by comparing the currents on the stationary and dropping electrodes for the same concentration of material and under the same electrolysis conditions. It was almost constant for the same potential value.

A change in the curvature of the meniscus on changing the potential of the mercury leads to a movement of the solution and as a consequence the conditions of linear diffusion break down to some extent. In order to

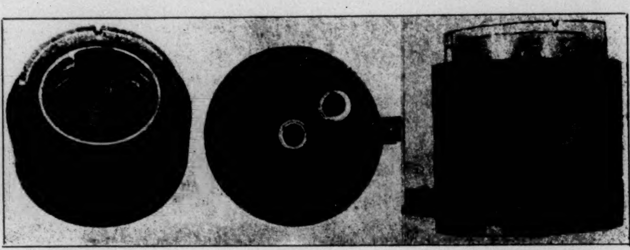


Fig. 1. Electrolytic cell consisting of two stationary mercury electrodes.

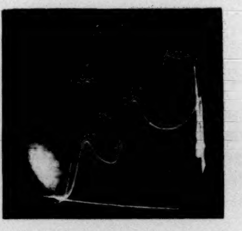


Fig. 2. Oscillogram of the anodic waves obtained at various concentrations of Cd^{2+} and Pb^{2+} in 1 N HCl on a stationary mercury electrode. $U_{=} = -1.0$ volt; $U_{\sim} = 0.944$ volt. The following are compared in the Fig.: supporting electrolyte 1 N HCl containing 27 μgCd^{2+}/ml and 53 μg Pb^{2+}/ml – lower curve; and the current for the same medium to which has been added 65 μg Cd^{2+}/ml and 120μg Pb^{2+}/ml – the upper curve. The straight line is the zero line. The upper curve is displaced slightly to the left and the peak for lead cannot be seen on it since it does not lie on the screen of the cathode ray tube.

avoid the effect of the curvature of the meniscus on the linear diffusion conditions it is necessary to increase the tube diameter to 2.0 cm; however, such a considerable increase in the surface area of the polarizing electrode would lead to a considerable increase in the cell dimensions on account of the increase in the area of the reference electrode. Such a huge cell is not always convenient in practice on account of the appreciable value of the capacity current. An indifferent electrolyte was poured into the electrolyzer. The original volume was 8 ml. To this was added dropwise from a buret a solution of a salt of the test element. After addition of each portion the test solution was electrolyzed at a definite time interval after mixing the solution, the rate (v) at which the potential was changed being – 3.4 volt/sec. The curves given below were recorded 1 minute after mixing the solution, during one sweep with a 9 sec delay. Dissolved oxygen was not removed from the solution. The values for the maximum current (I_p) of the test ion are the values obtained after correcting for the increase in the original volume following from additions of the standard solution.

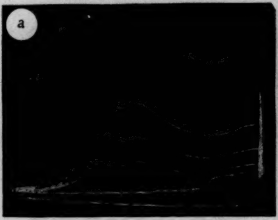
Quantitative determination of Pb^{2+} and Cd^{2+} in 1 N HCl.

The oscillogram of Cd^{2+} and Pb^{2+} in 1 N HCl (Fig. 2) was obtained during anodic polarization, when a constant negative potential ($U_{=} = -1.0$ volt) and a positive saw-toothed voltage ($U_{\sim} = 0.944$ volt) were applied to the cell.

Clearly defined anodic waves were observed on the oscillogram for Cd and Pb at values of φ_P and $\varphi_{P/2}$ of – 0.64 and – 0.67 volt (for Cd) and of – 0.38 and – 0.41 volt (for Pb). The difference between φ_P and $\varphi_{P/2}$ for the two elements is 0.03 volt, which is close to the theoretical value for reversible processes [6]. The calculation of the current of the second peak lead in this case, was carried out by means of the formula for the descending branch of the first wave (Cd^{2+}) for a reversible reaction [7].

The value of the current ($I_{reversible}$) on the descending branch of the first wave at a distance in excess of 2 volt from the first peak is determined by the relation:

$$I_{rever} = n_1 F S C_0 \sqrt{v} \sqrt{\frac{D}{\pi}} \sqrt{\frac{0,964}{(\varphi_1 - \varphi_2) + \frac{0,0056}{n_1}\left(\frac{T}{T_0}\right)}} \dots \quad (1)$$



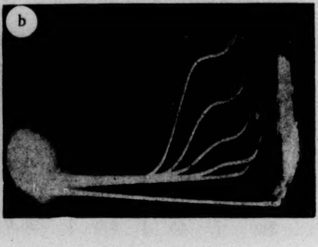


Fig. 3a. Oscillogram of the anodic waves of niobium in 23 N H_2SO_4 on a stationary mercury electrode. $U_{=} = -1.12$ volt; $U_{\sim} = 0.944$ volt.

Fig. 3b. Anodic current–voltage curves for various concentrations of Ti^{IV} in 23 N H_2SO_4 on a stationary mercury electrode. $U_{=} = -0.78$ volt; $U_{\sim} = 0.944$ volt.

Fig. 4. Oscillogram for anodic waves of uranium in 1 N HNO_3 on a stationary mercury electrode. $U_{=} = -0.87$ volt; $U_{\sim} = 0.944$ volt.

Here $I_{reversible}$ is expressed in amps, S in cm^2, C_0 in mole/ml, D in cm^2/sec; φ_1 and φ_2 are the potentials at which the peaks of the first and second waves appear. $T = T_0 + t$; $T_0 = 273°$, F is the Faraday number; and n_1 is the number of electrons which participate in the electrochemical reaction.

By substituting in Eq. (1) the following values: S = = 0.386 cm^2; $C_0 = 2.42 \cdot 10^{-7}$ mole/ml, v = 3.4 volt/sec, $D_{Cd^{2+}} = 7.16 \cdot 10^{-6}$ cm^2/sec, $\varphi_1 - \varphi_2 = 0.26$ volt and T = = 298°, we find that $I_{reversible}$ for $\varphi_2 = -0.38$ volt is equal to 184 μa, which on Fig. 2 corresponds to the line opposite the lead peak. The maximum current of Cd^{2+} on the lower curve is 336 μa. Thus, by means of the relation (1) it is possible to avoid the distortion of the second wave, while the true value of I_p for Pb^{2+} becomes 408 instead of 377 μa. The error arising from the distortion of the lead wave does not exceed 8%. For 65 μg Cd^{2+}/ml the value of I_p is 816 μa.

Quantitative determination of Nb^V and Ti^{IV} in 23 N H_2SO_4. A standard solution of Nb^V and Ti^{IV} in 23 N H_2SO_4 was prepared as before [8].

On the oscillogram (Fig. 3a) are shown the anodic waves for Nb^V in 23 N H_2SO_4 at $U_{=} = -1.12$ volt and $U_{\sim} = 0.944$ volt. The lower straight line is the zero line, the current of the supporting electrolyte (23 N H_2SO_4). On the upper curves, niobium waves obtained at various concentrations of niobium are added to the supporting electrolyte current. The niobium Nb^{III} peaks on the second, third, fourth, and fifth curves correspond to 125, 250, 385, and 770 μg Nb/ml. The following currents correspond to these concentrations: 138.7, 275.4, 428.4, and 856.8 μa. φ_p $Nb^{III} = -0.41$ volt which is close to the value of the potential for the niobium peak obtained on a dropping mercury electrode [9]. S = 0.363 cm^2.

At a higher positive potential a scarcely observable peak appeared on the current–voltage curves. This, presumably is caused by adsorption of Nb^{III} on the mercury surface. A similar peak is also observed on the anodic curves of niobium obtained on a dropping electrode [9].

In Fig. 3b are shown anodic current–voltage curves for various concentrations of Ti^{IV} in 23 N H_2SO_4. $U_{=} = -0.78$ volt, $U_{\sim} = 0.944$ volt. The sweep of the saw-shaped impulse changed from −0.78 to +0.164 volt. On this oscillogram (Fig. 3b) a comparison is made of the current of the supporting electrolyte – 23 N H_2SO_4 – and of the same medium to which various amounts of Ti have been added. The lower, straight line is the zero line. It is clear from Fig. 3 that with increasing titanium concentration there is observed a displacement of the whole curve to more negative potential values. It amounts to 0.13 volt. Such a significant shift of the

TABLE 1

Simultaneous Determination of Ti and Nb in 23 N H_2SO_4

Introduced into the solution		$\frac{C_{Nb}}{C_{Ti}}$	Found		Error, %	
niobium, μg/ml	titanium, μg/ml		niobium, μg/ml	titanium, μg/ml	niobium	titanium
38,0	304	0,125	39,4	299	+3,7	—1,7
50,0	100	0,5	52,4	98,6	+4,8	—1,4
125	83	~1,5	121,4	84,8	—2,9	+2,2
100	25	4,0	96,8	26,0	—3,2	+4,0
390	65	6,0	396,0	63,2	+1,5	—2,8

TABLE 2

Relation Between Current and Uranium Concentration in 1 N HNO_3

Uranium, μg ml	I_p, μa		Uranium μg ml	I_p, μa	
	anodic polarization, $U_= -0.87$ v $U_\sim$ 0.944 v	Cathodic polarization $U_= -$ 0.1 v, $U_\sim$ 0.944 v		anodic polarization, $U_= -0.87$ v $U_\sim$ 0.944 v	Cathodic polarization $U_= -$ 0.1 v, $U_\sim$ 0.944 v
30	20,4	—	416	282,9	—
60	40,8	—	480	315,8	342,0
120	81,6	89,5	960	—	689,0
240	158,6	177,7	1920	—	1364,0

TABLE 3

Relation Between Current and Cd^{2+} Concentration in 1 N HCl in a Flowing Cell. Anodic Polarization. $U_= = -0.9$ volt; $U_\sim = 0.944$ volt.

Cd^{2+}, μg/ml	On fresh mercury surface		On the same mercury surface which was not changed for:			
			12 hours		24 hours	
	I_p, μa	$I_{0.30}$, μa	I_p, μa	$I_{0.30}$, μa	I_p, μa	$I_{0.30}$, μa
0,1	0,54	—	0,52	—	0,55	—
0,2	1,04	—	1,06	—	1,05	—
0,3	1,53	0,74	1,55	0,76	1,58	0,77
0,4	2,14	1,01	2,18	1,03	2,15	1,02
0,5	2,69	1,23	2,64	1,22	2,73	1,25
1,5	8,12	3,58	8,05	3,51	8,17	3,61
2,5	13,43	6,15	13,56	6,28	13,49	6,21
6,0	32,54	14,46	32,32	14,24	32,68	14,39
10,0	56,00	23,52	54,89	22,80	55,11	23,20
20,0	108,40	47,92	110,50	49,25	110,20	48,25
40,0	220,00	93,51	217,50	91,52	224,09	94,02
50,0	283,00	117,52	275,30	109,82	279,20	111,41

curve cannot be related to an ohmic drop in potential, which in the given instance amounts to not more than 0.006 volt. It can be explained by the interaction of the anodic waves of Ti^{III} with the capacity current of the supporting electrolyte. Peaks for Ti^{III} are absent on the curve. However, when the capacity current is subtracted from the anodic waves of titanium, then a distinct Ti^{III} peak is observed at $\varphi_P = +0.16$ volt on the current–voltage curve, which indicates that the electrode reaction $Ti^{III} \rightarrow Ti^{IV}$ approximates to a reversible reaction.

For analytical purposes the method adopted was to measure from the capacity current, taken in the absence of Ti^{IV}, to the break on the anodic wave of titanium. Such an approximate measurement of the anodic

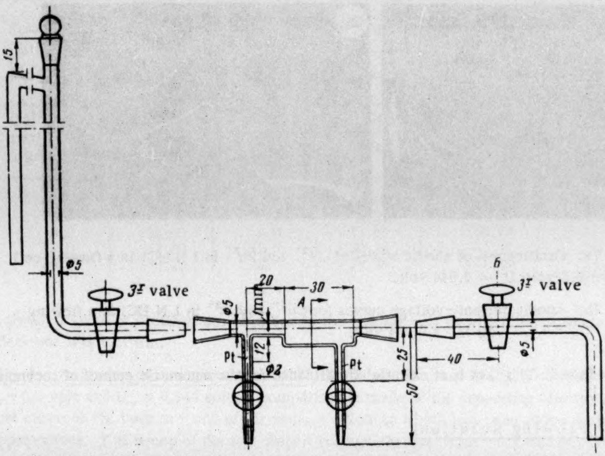


Fig. 5. Cell for analysis of plant streams.

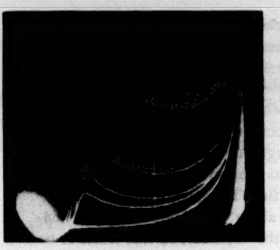


Fig. 6. Anodic current—voltage curves for various concentrations of Cd^{2+} in 1 N HCl in a flowing cell. $U_= = -0.9$ volt; $U_\sim = 0.944$ volt.

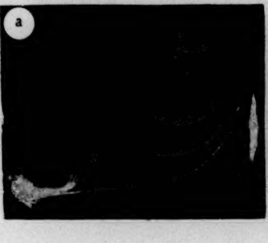
current of titanium preserves its proportionality to concentration, as can be seen from the oscillograms adduced (Fig. 3b). The Ti waves on the second, third, fourth, and fifth curves correspond, respectively, to 25, 65, 131, and 220 μg Ti/ml. The currents corresponding to these concentrations are 61.2, 163.2, 326.4, and 540.6 μa.

The difference of 0.6 volt between the potentials of the Nb and Ti peaks in 23 N H_2SO_4 indicates that it should be possible to determine these elements simultaneously. Results for the quantitative determination of Ti^{IV} and Nb^{V} in each other's presence on the basis of the anodic waves in 23 N H_2SO_4 are given in Table 1. The results given in Table 1 show that the deviation observed between the amounts taken and the amounts found, does not exceed the error usually obtained with a dropping mercury electrode.

Quantitative determination of U^{VI} in 1 N HNO_3. The oscillogram for UO_2^{2+} (Fig. 4) was obtained during anodic polarization, when $U_= = -0.87$ volt and $U_\sim = 0.944$ volt were applied to the electrolytic cell. On this curve a comparison is made of : the current of the supporting electrolyte 1 N HNO_3 — the first curve below, and the current of solutions containing various amounts of U — the top curves. The current—voltage curves are displaced relative to each other in a vertical direction. Curves 2, 3, 4, and 5 correspond, respectively, to 30, 60, 120, and 240 μg U/ml. The lower straight line is the zero line. Distinct anodic waves for quinquevalent uranium are observed on the current—voltage curves at $\varphi_p = -0.14$ volt. The values of I_p on the oscillogram in Fig. 4 and the results of other experiments are given in Table 2.

From the results given in Table 2 it is clear that the cathodic waves of sexivalent uranium are 8-12% higher than the anodic waves of quinquevalent uranium. Both the anodic and cathodic waves of uranium are linearly related to its concentration.

Numerous experiments which we have carried out show that the stable value of the current on a stationary mercury electrode is established rapidly (thanks to the short time taken to record the current—voltage curves)



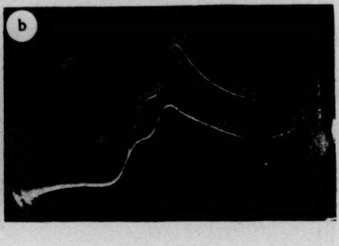


Fig. 7a. Oscillogram of anodic waves of Cd^{2+} and Pb^{2+} in 1 N HCl in a flowing cell. $U_{=} = -0.9$ volt; $U_{\sim} = 0.944$ volt.

Fig. 7b. Anodic current–voltage curves for Cd^{2+} and In^{3+} in 1 N HCl in a flowing cell. $U_{=} = -1.0$ volt; $U_{\sim} = 0.944$ volt.

and is readily reproduced. This fact is of essential significance for the automatic control of technological streams (plant streams).

Electrolysis of Flowing Solutions

Lewis and Overton [10], Bertram, Lerner, Petretic, Roszkowski, and Rodden [11], Alkire, Koyama, Hahn, and Michelson [12] have used a polarographic method for the continuous determination of uranium in flowing, dilute, technical solutions and in discarded, radioactive plant streams.

The use of a dropping mercury electrode is bound up with difficulties arising from the accumulation of a large amount of mercury contaminated with radioactive materials, the necessity of removing dissolved oxygen by means of an inert gas, the addition of surface-active materials to the test solution, and the presence of oscillations on the polarogram. It is impossible to suppress the oscillations on the polarograms significantly by using electrolytic condensers in parallel with the resistive load and the cell, when plant streams are being analyzed. The presence of oscillation leads to a decrease in the experimental accuracy of a determination. When a dropping electrode is used, it is necessary during the time the current–voltage curve is being recorded, that the test solution should be stationary for at least 2-3 minutes. This necessitates the introduction of an additional apparatus in the automatic line. The capillary which is immersed for a long time in an aggressive medium, e.g., in HNO_3, sucks the liquid inside, as a result of which its dropping period alters with time, leading to nonreproducible results. The use of a rubber tube also leads to contamination of the capillary, so that it has to be changed often.

In view of the drawbacks listed above which are associated with ordinary and derivative polarography for the continuous analysis of plant streams, it was deemed expedient to use oscillographic polarography for this purpose.

In Fig. 5 is shown an electrolytic cell for the analysis of plant streams in which mercury in a capillary with an internal diameter of 0.20 cm serves as the polarizing electrode. The large surface of the mercury in the convex part of the tube serves as the nonpolarizing electrode. The test solution was introduced into the cell either by means of a siphon or by a pressure difference at two points. The polarograms were taken without stopping the liquid. Linear voltage impulses were applied to the cell at 9 sec intervals at a rate of V = 3.4 volt/sec. An aliquot of the test element was added to 1 liter of indifferent electrolyte. After each addition of aliquot to the supporting electrolyte the test solution was passed several times through the cell at the rate of 258 ml/sec, only then was the oscillogram photographed. Dissolved oxygen was not removed from the solution. The mercury surface was not renewed for a long time. For repeated determination of the same concentration of the test element, the cell was carefully washed by passing indifferent electrolyte through it after each series of experiments. In order to prevent penetration of electrolyte between the mercury and the glass, the internal surface of the cathode compartment was smeared with silicone. The area of the electrode was determined by comparing the currents for the same concentration of the material under the same electrolysis conditions in the "flowing" cell and on the dropping mercury electrode.

TABLE 4

Relation Between the Maximum Current of Cd^{2+} and Pb^{2+} and Their Concentration in 1 N HCl in a Flowing Cell. Anodic Polarization $U_{=} = -0.9$ volt; $U_{\sim} = 0.944$ volt. The Mercury Surface was not Renewed for 26 Hours

Cd^{2+} concentration, μg/ml	I_p, Cd^{2+}, μa	Pb^{2+} concentration, μg/ml	Approximate value of I_p for Pb^{2+}, μa	True value of I_p for Pb^{2+}, calculated by means of modified formula (1), μa
0,5	2,71	0,5	1,49	1,59
1,5	8,28	1,5	4,39	4,68
6,0	33,90	6,0	17,98	18,73
12,0	67,80	12,0	35,96	37,67
24,0	139,20	24,0	71,42	77,23

Below are shown a series of oscillograms obtained in the flowing cell in which the diameter of the polarizing mercury electrode was 0.27 cm.

Quantitative determination of cadmium in 1 N HCl. In the oscillogram in Fig. 6 obtained during anodic polarization ($U_{=} -0.9$ volt and $U_{\sim} = 0.944$ volt) a comparison is made of the supporting electrolyte (1 N HCl) current, – the first curve on the bottom – and of the same medium to which had been added various amounts of Cd^{2+} – the upper curves. The sweep of the saw-shaped voltage changes from -0.9 volt to $+0.044$ volt. Clear-cut Cd^{2+} peaks are observed on the current–voltage curves, with the exception of the upper peak, which does not lie on the screen of the cathode ray tube. The ohmic potential drop does not exceed 0.006 volt, since φ_p is displaced insignificantly to more positive potential value for various Cd^{2+} concentrations.

Curves 2, 3, 4, and 5 correspond, respectively, to: 6.0, 10.0, 20, and 50 μg Cd^{2+}/ml. The following values of I_p correspond to these concentrations: 32.54, 56.0, 108.4, and 283.0 μa.

The concentration of the test element can also be determined from the current of the descending branch of the polarographic waves at a distance greater than 0.2 volt from the peak, as follows from the equations given below which are derived from a stationary liquid [7]. The following values were obtained for the current at distances of 0.20, 0.27, 0.30 volt from the maximum:

$$\left.\begin{aligned} I_{0,20} &= 1,143\cdot 10^{5}\cdot n_1 S C_0 \sqrt{D}\sqrt{V} \\ I_{0,27} &= 1,000\cdot 10^{5}\cdot n_1 S C_0 \sqrt{D}\sqrt{V} \\ I_{0,30} &= 0,942\cdot 10^{5}\cdot n_1 S C_0 \sqrt{D}\sqrt{V} \end{aligned}\right\} . \qquad (2)$$

The values of the current (I) at a distance of 0.3 volt from the peak are determined in Fig. 6. The corresponding points on the curves are marked by the dotted line. The following values were found for the same Cd^{2+} concentration: 14.46, 23.52, 47.92, and 117.52 μa.

A comparison of the value found for I, with the theoretical values calculated by means of formula (2) for 10 μg Cd^{2+}/ml, shows that the deviation between the two values amounts to 20% ($S = 0.194$ cm² and $I_{0.30} = 18.04$ μa instead of 23.52 μa). This significant difference between the experimentally determined current and the theoretically calculated value is caused by the flow of the liquid. Despite such a significant deviation, the oscillogram in Fig. 6 shows that in the flowing liquid, the current of the descending branch of the wave is linearly proportional to the cadmium content of the solution.

Table 3 contains results for the determination of Cd^{2+} in 1 N HCl; they were obtained on fresh mercury and on mercury whose surface had not been renewed.

It is clear from the results given in Table 3 that the anodic waves for cadmium measured on the basis of the peak height of the descending branch of the wave, are directly proportional to the concentration, both on a fresh mercury surface and on the surface of mercury which had been subjected to prolonged electrolysis.

Quantitative determination of Pb^{2+}, Cd^{2+}, and In^{3+} in 1 N HCl. On the oscillogram in Fig. 7a are shown anodic curves for various concentrations of Cd^{2+} and Pb^{2+} in 1 N HCl for $U_= = -0.9$ volt and $U_\sim = 0.944$ volt. The potential sweep alters from -0.9 volt to $+0.044$ volt. The first curve from below is the current of the supporting electrolyte – 1 N HCl. Cd and Pb waves are added to the supporting electrolyte current on the upper curves. The first peak on the left corresponds to Cd^{2+}, while the second corresponds to Pb^{2+}. $\varphi_p Cd = -0.64$ volt; $\varphi_p Pb = -0.38$ volt. The coincidence of the peak potentials of cadmium and lead with $\varphi_p Cd^{2+}$ and Pb^{2+} on a dropping and on stationary electrodes shows that electrolysis in a flowing cell does not distort the nature of the current–voltage curves (compare Figs. 2 and 7a). The oscillogram in Fig. 7a was obtained on the same mercury surface as that used for Fig. 6, but it was not renewed for 26 hours in the course of a given series of experiments. The Cd and Pb peaks on curves 2, 3, and 4 were taken for a solution of 1 N HCl containing, respectively, 6, 12, and 24 μg of Cd^{2+} and Pb^{2+}/ml. The following values of I_p were obtained for Cd: 33.90, 67.80, and 139.2 μa. Although the mercury surface was not renewed for a long time, the coincidence observed between the values of the maximum current of Cd^{2+} with $I_p Cd$ in the absence of Pb (see Table 3) testifies to the good reproducibility of the results.

Measurements of the maximum current of Pb in Fig. 7a, starting from the minimum on the ascending curve to the peak, gave the following values of I_p for concentrations of 6, 12, and 24 μg Pb^{2+}/ml: 17.98, 35.96, and 71.42 μa. Although such a measurement technique does not take into account distortion of the Pb wave by the preceding Cd wave, and does not give the true value of the current, it is nevertheless suitable for analytical purposes, since a linear relationship is observed between the current and the Pb^{2+} concentration. The true values of I_p should be 5-8% higher than the values given above.

Results for the simultaneous determination of Cd^{2+} and Pb^{2+} in 1 N HCl are given in Table 4. It follows from these results that it is possible to carry out a quantitative determination of Cd and Pb in a flowing cell, since the currents for Pb^{2+} and Cd^{2+} are linearly proportional to the concentrations. The lead content of the test solution can be evaluated by measuring the peak height from the level of the minimum preceding it.

Figure 7b, which was obtained during anodic polarization ($U_= = 1.0$ volt, $U_\sim = 0.944$ volt), shows that the flowing cell is also suitable for the simultaneous determination of In and Cd in 1 N HCl. The first wave from the left corresponds to Cd^{2+}, while the second corresponds to In^{3+}. Because of the proximity of the half-wave potentials of Cd and In in 1 N HCl, the In^{3+} peak on the current–voltage curves is distorted by the preceding Cd^{2+} wave. However, this does not interfere with the quantitative determination of indium, as long as the In^{3+} content of the solution is evaluated by measuring the peak height from the level of the break preceding it on the curve. The lower curve was taken with 1 N HCl containing 5 μg Cd^{2+}/ml and 6.5μg In^{3+}/ml. $I_p Cd^{2+} = 28.08$ μa; $I_p In^{3+} = 21.21$ μa. The upper curve was obtained for the same medium to which had been added 10 μg Cd^{2+}/ ml and 10.5 μg In^{3+} /ml. For these concentrations of Cd and In the corresponding values of I_p were 56.16 and 34.32 μA.

Quantitative determination of uranium in the presence of Fe^{3+}. The oscillogram for U^V in Fig. 8 was obtained during anodic polarization ($U_= = -1.0$ volt, $U_\sim = 0.944$ volt) on a mercury surface which had been in contact with 1 N HNO_3 for a long time (96 hours). The following curves are compared on this Fig.: the current of the supporting electrolyte – 1 N HNO_3 – the first curve from the bottom, and the current for a solution containing various amounts of U^{VI} and Fe^{3+} – the upper curves. The ratio of Fe to U is 3.

The current–voltage curves are artificially shifted relative to one another in a vertical direction, and, in addition, the two upper curves are shifted slightly to the left. The bottom line is the zero line. A wave resulting from the presence of Hg ions in 1 N HNO_3 appears on the current of the supporting electrolyte. It almost coincides with the U wave. Accordingly, measurement of the peak heights of uranium in the given case was carried out from the level of the supporting electrolyte wave. Curves 2, 3, and 4 correspond to 58.4, 116.8, and 233.6 μg/ml. For these U concentrations the following values were obtained for I_p: 13.44, 25.76, and 51.80 μa. A series of experiments was carried out on the determination of U in the presence of Fe^{3+}: the concentrations of the latter are considerably higher than the concentration of U^{VI} in the test solution. Results of the measurements of the peak heights are given in Table 5.

It is clear from the results given in Table 5 that the anodic currents of U are linearly proportional to its concentration both on a fresh mercury surface and on a mercury surface which has been in contact with the test solution for a long time. The presence of iron in the test solution in an amount which is four times the uranium concentration, does not interfere with the quantitative determination of the latter.

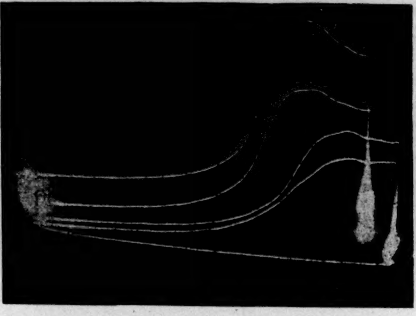


Fig. 8. Anodic curves for uranium in 1 N HNO_3 containing Fe^{3+} in a flowing cell. $U_{=} = -1.0$ volt, $U_{\sim} = 0.944$ volt.

TABLE 5

Relation Between the Maximum Current and U Concentration in 1 N HNO_3 in a Flowing Cell in the Absence and in the Presence of Fe^{3+}

On a fresh mercury surface			On a mercury surface which has not been renewed for 96 hours		
U, μg/ml	Fe/U	I_p, μa	U, μg/ml	Fe/U	I_p, μa
250	0	57,5	152	0	35,0
400	0	87,5	196	4	45,0
430	3	97,5	261	4	60,0
750	0	169,3	353	3	81,2
1050	2	230,8	522	4	120,0
1430		325,9			

SUMMARY

Oscillographic polarography can be used for the automatic control of production solutions; it possesses **high sensitivity** and selectivity, and the results obtained are reproducible.

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THE USE OF A "SOUNDING" ARC FOR FOLLOWING THE PASSAGE OF MATERIAL INTO DC ARC PLASMA

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The reproducibility of the results of the spectrographic determination of elements depends to a large extent on variations in the operational conditions of the spectrum excitation source, and on sporadic changes in the conditions under which the elements pass from the sample into the source plasma. Meanwhile, when an analysis is carried out, even when the electrical parameters of the arc (current strength and voltage) are kept strictly constant, the variations mentioned above in the conditions of the evaporation of the elements from the sample and their excitation in the plasma still remain without reliable control, and, accordingly, they cannot be taken into account during an evaluation of the accuracy of the results obtained.

In order to control the passage of the elements into the arc plasma, Rusanov [1] suggested a method based on measuring the potential difference at the ends of the source electrodes.

In the work described here an attempt was made to solve this problem by another method – by supplementing existing excitation sources (e.g., a dc arc) by a setup which would react more or less sensitively to changes in the conditions of the passage of the elements into the plasma, and would allow these processes to be followed by means of the simplest, e.g., sonic signal. Such a "sounding" arc [2] would open up a way for a more accurate experimental study of the processes occurring in the source, and its use in spectrographic practice would favor an increase in the reproducibility and accuracy of the analysis.

The present article includes some results obtained recently which illustrate the possibility of using a "sounding" arc for following the passage of material into the source plasma.

A schematic diagram of the source is shown in Fig. 1. To a dc arc is connected an oscillating circuit, the natural frequency period of which $T = 2\pi\sqrt{LC}$ lies within the range $2 \cdot 10^{-2}$ to $5 \cdot 10^{-5}$ sec. Accordingly, the vibrations of the plasma with this period are strengthened and appear externally in the "sounding" arc, which can be picked up aurally or recorded and analyzed quantitatively by means of an oscillograph, magnitophone, or a sound generator. In order that the ac component of the arc current is not branched into the main circuit, a high frequency choke is included in the "sounding" circuit. In order to increase the sounding power of the arc, an additional capacity C' is connected in parallel with the arc. In the circuit which we used in the work described here the self-inductance L was varied within the range 0.1 to 0.25 mH, while the capacities C and C' were varied within the limits 8 to 18 and 5 to 16 μF, respectively. The sounding intensity of the arc was measured by means of the cathode voltmeter of the sonic generator.

In order to increase the accuracy of the measurements of the duration and intensity of the sounding of the arc during an analysis, it was recorded on a magnetic tape. Such a technique is particularly effective for measuring very short time breakdowns in the conditions of the "sounding" source. It allows one to record and measure

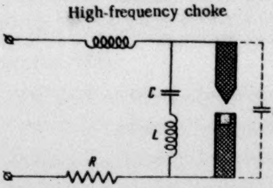

Fig. 1. Schematic diagram of a "sounding" arc.

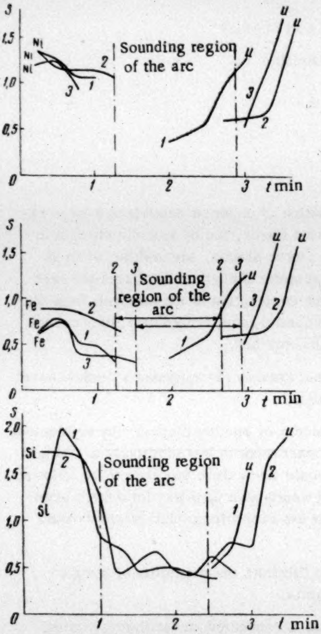

Fig. 2. Blackening-changing curves for the lines of nickel (at the top), iron (in the middle), and silicon (below) during their evaporation from uranoso uranic oxide on the cathode of a dc arc under ordinary conditions (1) and under the "sounding" conditions of the arc, for two values of the self-inductance L = 0.1 mH (2) and 0.25 mH (3).

reliably the breaks in the sounding of the arc of the order of fractions of a second. The use of such a magnetic recording may also prove useful for synchronous "scoring" of the matching frames during kinematographic recording of processes occurring in the arc plasma with time.

In order to illustrate some of the characteristics of a "sounding" arc, let us consider for example the evaporation of Fe, Ni, Si, and Al from uranoso uranic oxide in the presence of Ga_2O_3 and NaCl, which often, for various reasons, may occur in the sample being tested during analysis. For convenience in carrying out the experiments described (increasing the evaporation time of the impurities from difficultly volatile bases) the sample was not evaporated on the anode, but on the cathode of a dc arc from a crater 4 mm deep. The current was 12 amp. In Fig. 2 a comparison is made of the curves for changes in the blackening of the analytical lines Ni, Fe, and Si with time, during evaporation of these impurities from uranoso uranic oxide in a dc arc under ordinary conditions (before switching on the "sounding" circuit) and under the "sounding" conditions of the arc at two different values of the self-inductance. The dotted lines on the diagrams mark out the "sounding" region of the arc. As is evident, under the experimental conditions chosen the arc sounds in the time intervals following the almost complete evaporation of Fe and Ni from the sample, and precedes the intensive passage of the difficultly volatile base into the plasma. On going from the ordinary arc to a "sounding" arc there is observed a small additional hold up* during the passage of uranium into the arc, the magnitude of this hold-up being dependent on the value of the self-inductance of the oscillating circuit. The latter value also affects the shape of the evaporation curve of the element. Both these effects are manifested fairly clearly on the evaporation curves of Ni and Fe, and is much less clearly manifested on the curves relating to Si. Thus, in the case considered, the use of a "sounding" arc leads to a small extension of the interval separating the region of intense evaporation of the test impurities and the base from the sample, and also permits objective control (from the sound) during the analysis, of the time of evaporation of the main mass of nickel and iron from the test sample.

As experiments have shown, a "sounding" arc also permits one to fix accidental breakdowns in the normal passage of the elements – impurities into the source plasma, which may occur during the analysis of actual samples. Proof of this may be obtained by

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* One of the reasons for this phenomenon may be a small decrease in the source temperature during the "sounding" period of the arc, which, as an approximate evaluation showed, may be 200-300°.

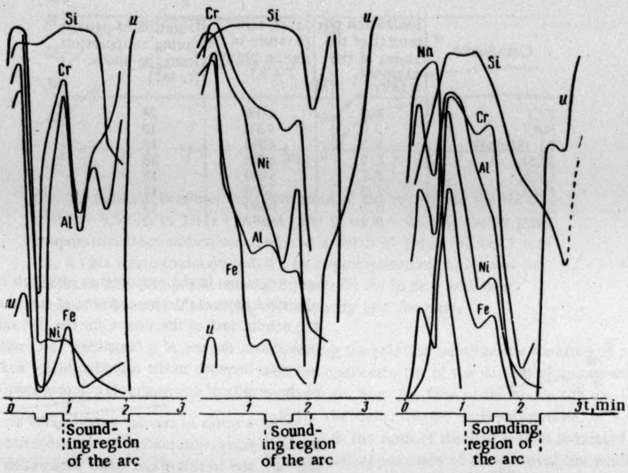

Fig. 3. Curves of the changes in blackening of the lines of Fe, Al, Ni, Cr, Si, and Na during the evaporation of these elements from various samples of uranoso uranic oxide on the cathode of a "sounding" arc. Below is shown graphically the character of the "sounding" arc during the experiment. The dotted lines mark out the "sounding region" during normal evaporation of impurities.

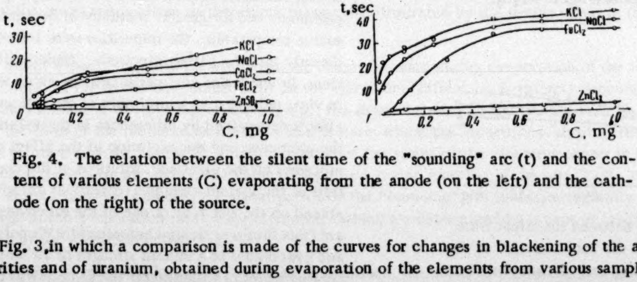

Fig. 4. The relation between the silent time of the "sounding" arc (t) and the content of various elements (C) evaporating from the anode (on the left) and the cathode (on the right) of the source.

considering Fig. 3, in which a comparison is made of the curves for changes in blackening of the analytical lines of the impurities and of uranium, obtained during evaporation of the elements from various samples, with the curve of a sounding arc during an experiment. It is clear that both the accidental holdup in the evaporation of Al, Ni, Cr, and Fe which occurs during an experiment, and to which the curves in Fig. 3 (on the left) relate, and the sudden increase in the content of all or some of these elements in the plasma, which occurs after evaporation of the main mass of impurities in the two other cases (Fig. 3 in the middle and on the right), can be equally clearly recorded by means of a "sounding" arc. In the first case the arc starts to sound unexpectedly, while in the other two cases—on the contrary—there are observed more or less continuous pauses which are timed to the region of the "sounding" source. In practice this enables the analytical technique to be improved by two methods. It is possible to choose the exposure time for the spectrograms "by sound," and in this way factually take into account the characteristics of the passage of the test elements into the source plasma during the analysis of an actual sample. When a constant exposure time is used, the use of a "sounding" arc allows one to exclude from consideration (on the basis of experimental results) the results of measurements of those

TABLE

Compound	Ionization potential of the atoms of the element, E (ev)	Mean temperature of the source plasma T (°K)	Duration of pause during evaporation from the anode (t, sec)
KCl	4,3	4100	28
NaCl	5,0	4300	19
Al (Metal)	5,9	4600	18
Al_2O_3	5,9	4600	28
$CaCl_2$	6,2	4800	16
$FeCl_3$	7,8	5300	14
SiO_2	8,1	5500	13
$ZnCl_2$	9,4	6200	3

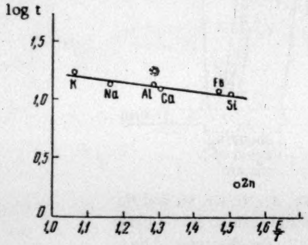

Fig. 5. Relation between log t and E/T during the evaporation of the same amount (1 mg) of various elements on the anode of a "sounding" arc. The dot surrounded by dashes belongs to Al_2O_3.

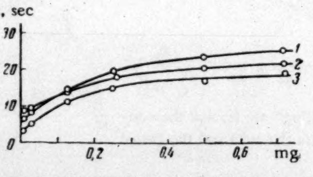

Fig. 6. Relation between the silent time of the arc (t) and the concentration of the impurity (C) during evaporation of sodium chloride from the surface of an anode (3) and from the crater of the electrode at a depth of 5 mm (2) and 7 mm (1).

spectrograms in the preparation of which there were observed appreciable breakdowns of the normal "sounding conditions" of the source for the test samples. In both cases, the use of a "sounding" arc will obviously favor an increase in the reproducibility and reliability of the results of spectrographic determinations.

In a series of special experiments an attempt was made to study systematically the properties of a "sounding" arc and to relate the basic parameters characterizing its operation — the intensity and duration of the sound signals or pauses — to the concentrations of the impurities evaporating on the electrode, their volatility, the values of the ionization potential of the atoms, the mean temperature of the source, the intensity of diffusion processes on the electrode and the nature of the bonds between the impurity atoms and the crystal lattice of the main material, and other factors. In order to simplify the experiments and for greater accuracy in determining the source temperature, the impurities were introduced directly into the carbon electrode. Under such conditions, in one series of experiments, in which was borne in view reduction to a minimum of the influence of effects determined by differences in the volatility of the elements, and the exclusion of the effect of diffusion processes on the electrode, solutions of the corresponding salts of the various elements (mainly as chlorides) were placed on the flat face of one of the electrodes of a dc arc (this face was treated beforehand with polystyrene) and evaporated at a current strength of 12 amp. In another series of experiments the sample was placed at different depths on the bottom of the channel of the carbon electrode, and, after filling the remaining volume of the channel by carbon powder, it was evaporated under the same conditions. The parameters of the oscillating circuit and the value of the interelectrode gap were chosen so that in the absence of appreciable amounts of the impurities in the source plasma, the arc sounded continuously. The impurities were evaporated at two electrode temperatures from the cathode and the anode of a dc arc. During the passage of known and varying amounts of the impurity elements, depending on the element, into the source plasma, the sounding of the arc stops after a certain time. The object of the investigation was to establish the relation between the duration of these pauses and the properties of the evaporating elements and some parameters characterizing the excitation source or the evaporation conditions of the materials on the electrodes. In Fig. 4 are shown curves

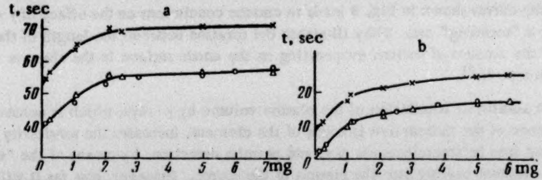

Fig. 7. Relation between the silent time of the arc (t) and the Na content (r = 0.98 A) in Th (r = 0.95 A) and in Be (r = 0.34 A) during their evaporation from carbon electrodes at a depth of 7 mm (a) and 1 mm (b). ×) Na was introduced into Th by coprecipitation; Δ) Na was introduced into Th by mechanical mixing; ●) Na in Be – whichever method is used for introducing the impurity into the base.

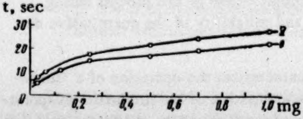

Fig. 8. Curve $t = f(C)$ for sodium in the absence (1) and in the presence (2) of the γ -active isotope of the element (Na^{24}) in the sample.

expressing the relation between the duration of a sound pause and the concentration of the various elements during their evaporation from the face of the anode (on the left) or cathode (on the right) treated with polystyrene, of a dc "sounding" arc in the form of the compounds indicated on the Fig. The general appearance of these curves are similar for the various elements. In all cases, at relatively low contents of the elements, there is observed a fairly sharp and almost linear relation between the duration of the pause and the amount of the element evaporating from the electrode. During evaporation of large amounts of an element (greater than 0.2-0.3 mg) the slope of the line which expresses the relation between the duration of a pause and the concentration decreases. The relation between the duration of the silent period of the "sounding" arc and the ionization potential of the atoms of the evaporating elements, their volatility, and the mean temperature of the source plasma are illustrated by the results given in the Table and in Fig. 5.

As one might expect, the time for which the arc ceases to sound during evaporation of the same amount of various elements (1 mg in the case considered) on the electrodes differs. It is strongly dependent on the volatility of the element or of its compounds (see, e.g., the results relating to the readily volatile $ZnCl_2$ or aluminum in the form of the metal or its oxide), while in cases where the volatility is similar, the silent period is determined primarily by the ease with which ionization of the atoms of the elements occurs in the plasma. In the latter case, as experiment shows, the value of log t is a linear function of the ratio E/T. During evaporation of a sample from the cathode, the silent period of the "sounding" arc increases regularly in accordance with the change in the evaporation rate of the elements, which we determined by means of labelled atoms, from the depth of the electrode crater (Fig. 6).

Under conditions such that formation of a melt is excluded, the value of t also depends on the nature of the entry of the impurities into the crystal lattice of the base material (Fig. 7). In those cases where isomorphous penetration of the impurity atoms into the crystal lattice of the base is possible (Na in Th, Fig. 7), there is observed a difference in the duration of the sound pause (t) during evaporation from the crater of a carbon electrode of the same amount of impurity introduced into the base chemically or by mechanical mixing. For ratios of the ionic radii of the impurity atoms to those of the base material (Na in Be, Fig. 7) which are unfavorable from the point of view of isomorphism, the relationship indicated between the character of the evaporation of the impurity and the method whereby it is introduced into the base material is not observed. Thus, in experiments with a "sounding" arc it is again possible to confirm the conclusion reached as to the effect of the trapping of the impurities by the crystal lattice of the base, on the nature and rate of their evaporation, conclusions which some of us arrived at earlier [3, 4] by means of labelled atoms.

Examination of the curves shown in Fig. 8 leads to curious conclusions on the effect of γ -radiation on the operation conditions of a "sounding" arc. They illustrate the relation between the length of the silent period of the "sounding" arc and the amount of sodium evaporating on the anode surface in the absence and in the presence of the γ -active isotope Na^{24}.

As is evident, the additional irradiation of the plasma volume by γ -rays, which is achieved in the second case thanks to the presence of the radioactive isotopes of the element, increases the sensitivity of the "sounding" arc to the sodium passing into its interelectrode gap, and permits detection, by means of the "sound" signal, of smaller amounts of the element passing into the plasma of the source. However, how far it will be possible to increase the sensitivity of the determination of elements by means of a "sounding" arc, using the effect detected, and how effective will prove irradiation of the interelectrode gap of the "sounding" arc by ionizing radiation or by an electron beam, can only be shown by further experimental work.

The authors wish to thank V. A. Kosterina for help in the experimental work.

SUMMARY

It has been shown that the use of a "sounding" arc permits one to follow the passage of materials into the source plasma, and to record the accidental (random) breakdown of the normal course of this process during spectrographic analysis. It can be used for increasing the reproducibility and reliability of the quantitative determination of elements.

It has been shown experimentally that the main parameter which characterizes the operation of a "sounding" arc – the duration of the sound signals and pauses – depends on the concentration of the impurities evaporating on the electrode, their volatility, the ionization potential of the atoms of these elements, the source temperature, and some other factors. In a number of cases the authors have succeeded in establishing the nature of these relationships.

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* Original Russian pagination. See C. B. Translation.

DETERMINATION OF POTASSIUM PRESENT AS AN IMPURITY IN RUBIDIUM CHLORIDE BY A FLAME PHOTOMETRIC METHOD

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There are no reliable and rapid methods for the determination of potassium, rubidium, and cesium in each other's presence, particularly when one of these elements is present in considerable excess. Hitherto, several papers have been published on the flame photometric analysis of mixtures of potassium, rubidium, and cesium [1-3]. Poluéktov and Nikonova [3] used the method of additions for the determination of lithium, sodium, potassium, and rubidium in cesium salts. However, the method of additions is only applicable for very low concentrations of the elements to be determined. For potassium the limits of application are 0.004-0.005% and for rubidium and cesium 0.01-0.008%.

Our work was carried out on a ISP-51 spectrograph provided with a FÉP-1 photoelectric setup. The latter consists of an output collimator connected to a ISP-51 spectrograph with an amplifier and a recording mechanism for recording the spectra of weak radiation (luminescence, combination scattering). When a FÉU-17 photoelectric multiplier is replaced by a FÉU-22 or a VÉI multiplier, then the setup becomes suitable for the analysis of mixtures of the alkaline metals. The prism system of the ISP-51 spectrograph is rotated by means of the electric motor of the FÉP-1 setup, the motor being connected via a cord shaft with the handle of the rotating mechanism of the spectrograph prism. The readings of the rotational angle of the prism are carried out on the drum scale of a setup rotating synchronously with scales similar to that of the reading drum of the spectrograph. The linear dispersion of the setup for λ 471.3 mμ does not exceed 32 A/mm. The rate at which the ribbon of the ÉPP-09 potentiometer moves can be regulated from 60 to 9600 mm/hour. The maximum amplifying factor of the dc amplifier is 10^6. The setup, in contrast to self-made spectrophotometers based on a UM-2 monochromator, permits determinations to be carried out by the internal standard method.

Spectrophotometers operating on the internal standard method are usually provided with two photomultipliers or photoelements (in the photometers), one of which records the intensity of the impurity line, and the other records that of the internal standard. Shifting the spectrum in front of the output slit of the setup and simultaneously synchronizing the focussing of the various parts of the spectrum on the photomultiplier cathode can be avoided by using one photomultiplier. The atomizer was fed with compressed air from a small compressor fitted with a reservoir. For an air pressure in front of the atomizer of 0.28 kg/cm^2, the latter required 0.04 ml/sec of the test solution. The acetylene pressure was kept at a level of 110-160 mm water. The pressure of the air and acetylene was kept constant during a determination. The input slit varied from 0.03 to 0.08 mm and the output slit from 0.05 to 0.1 mm, depending on the experimental conditions. The rate at which the potentiogram was shifted was 360 mm/hour. The dark current was compensated by an appropriate setting of the zero of the setup's power supply potentiometer. In order to avoid lowering the sensitivity of the photoelectric multiplier during its first minutes of operation, the photoelectric setup was switched on for 15-20 minutes beforehand, while at the same time a solution containing approximately the maximum (from the relevant measurement) concentration of the impurity to be determined, was sprayed into the flame.

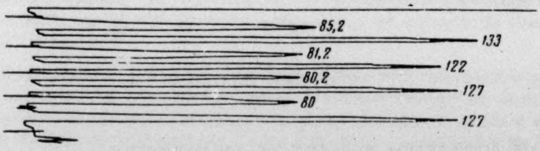

Fig. 1. General appearance of a potentiogram. The small peaks are recordings of the intensity of the spectral line of the impurity, while the large peaks are recordings of the weakened intensity of the spectral line of the internal standard. The figures at the peak tips indicated the values of their ordinates (in mm).

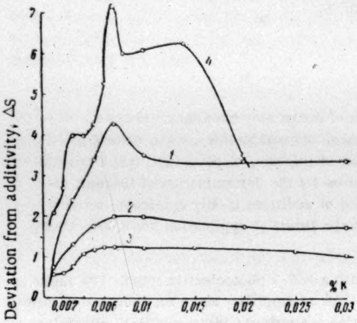

Fig. 2. Δ-Diagram. 1 and 2) Curves illustrating the deviation from additivity for a RbCl concentration of 6 g/100 ml for inlet and outlet slits of 0.1/0.025 mm and 0.07/0.02 mm, respectively; 3 and 4) curves for the deviation from additivity for a RbCl concentration of 4 g/100 ml, using inlet and outlet slits of 0.07/0.02 mm and 0.15/0.03 mm, respectively.

The rubidium chloride used for preparing the standards was purified from potassium by the chlorostannate method. The amount of potassium remaining (0.0001-0.0003%) was determined by the method of additions, and was taken into account when working out the analytical results. Chemically pure-grade potassium chloride was recrystallized twice from water and was checked for freedom from rubidium and cesium.

The standard solutions were prepared by dissolving 2.2 g of rubidium chloride in 50 ml of distilled water (which was checked for absence of potassium). Nine ml lots of this solution were transferred by means of a calibrated pipet into small beakers; to each of these beakers was then added 1 ml of potassium chloride solution of varying concentrations. Each beaker (standard) thereby contained 4 g RbCl/100 ml. The standards were successively measured photometrically by means of the resonance lines – 766.5 mμ for potassium and 780 mμ for rubidium. The relative intensity rather than the absolute intensity of the impurity line was measured, using the main element of the standard as reference element. In order to cut down the intensity of the spectral line of the internal standard (otherwise the pen of the photoelectric setup potentiometer went off the scale) a neutral filter type NS-8, 4 mm thick, was used. For a wavelength of 640 mμ the transmission of the filter was not greater then 7.6%. The filter indicated is included in the kit of the SF-4 spectrophotometer. Other types of neutral filters can also be used. The filter was fitted into a special mounting, which in turn was fitted onto the tube of the inlet slit before exposing the line of the internal standard to the input slit of the photoelectric setup. For each standard, the line of the impurity and the line of the internal standard was measured photometrically in turn not less than three times. The mean arithmetic values of the potentiogram ordinate were taken for calculation. The most suitable lines of the internal standard for potassium would be the rubidium spectral lines 761.9 mμ or 775.8 mμ. Unfortunately, the acetylene-air flame does not cause the appearance of these lines on the potentiogram.

In order to calculate the concentration it is desired to determine, we used a calibration curve which relates the logarithm of the relative intensity ($\log I_{\text{standard}}/I_{\text{internal standard}}$) to the logarithm of the concentration ($\log C_{\text{standard}}$), where I_{standard} is the average reading of the spectrophotometer for the standard, $I_{\text{internal standard}}$ is the reading for the internal standard, and C_{standard} is the concentration of the standard.

TABLE 1

Results Used for Constructing the Calibration Curve

Standards		1	2	3	4	5	6	7	Sample A
Potassium content of the standard, %		0,0021	0,0031	0,0051	0,0071	0,01	0,015	0,020	0,0054
Mean value of I_K/I_{Rb}	Line 1	0,309	0,345	0,516	0,726	1,110	1,442	1,807	0,609
	Line 2	0,357	0,364	0,597	0,816	1,103	—	—	0,650

TABLE 2

Results of Analyses by the One-Standard Method

Potassium content, %		Mean value of I_K/I_{Rb}		Potassium found in the sample, %	Error, % (relative)
standard	sample	standard	sample		
0,007	0,0054	0,692	0,586	0,006	11,1
0,007	0,0054	0,728	0,487	0,0046	14,8
0,007	0,0054	0,764	0,590	0,0054	0,0
0,005	0,0054	0,640	0,700	0,0056	3,7
0,005	0,0054	0,579	0,590	0,0052	3,7
				Mean error, % (relative)	6,6

TABLE 3

Effect of Various Impurities on the Determination of Potassium in Rubidium Chloride

Impurity introduced	Potassium content of the sample, %	Concentration of the impurity in the sample, %				
		0,001	0,01	0,05	0,1	0,5
		potassium found in the sample, %				
Na	0,005	0,004	0,005	0,005	0,005	0,005
	0,008	0,008	0,008	0,008	0,007	0,007
Cs	0,005	0,005	0,005	0,005	0,005	0,005
	0,008	0,008	0,008	0,008	0,008	0,008
Ca	0,005	0,005	0,005	0,005	0,005	0,006
	0,01	0,009	0,01	0,01	0,009	0,009
Mg	0,005	0,005	0,005	0,005	0,005	0,005
	0,01	0,009	0,008	0,009	0,008	0,008

Note: The experimental results were rounded off to the first significant figure.

By measuring the intensity of the impurity line ($I_{impurity}$) with respect to the weakened intensity of the internal standard ($I_{internal\ standard}$), from $\log I_{impurity}/I_{internal\ standard}$), it is possible to find on the curve log $C_{impurity}$, i.e., the concentration it is required to determine. By using a logarithmic scale it is possible to simplify all the calculations. The general appearance of one of the potentiograms is shown in Fig. 1.

It was observed that with increasing concentration of the main material in the sample, the growth of the emission of the test element reaches a definite limit, beyond which there is no further change in the emission. Changes in the emission of the impurity is observed at a concentration of the main element which does not exceed 1 g/100 ml. Similar observations, but only on cesiumsalts, were made by Poluěktov and Nikonova [3]; the intensity of the potassium (0.0005-0.05%) radiation and rubidium (0.001%) radiation did not change, starting from a 0.5% solution of cesium chloride.

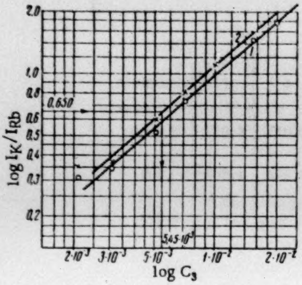

Fig. 3. Calibrations lines.

The effect of the main alkali metal of the sample on the radiation intensity of the other alkali metal present as an impurity, and which it is desired to determine, is particularly clearly seen on constructing a Δ-diagram. Should potassium chloride only be present in the test solution, then the spectrophotometer would give a reading E_K, while a solution of rubidium chloride only would give a spectrophotometer reading of E'_{Rb} (when the spectrophotometer is adjusted for the spectral line of potassium). When potassium and rubidium chloride are present together one would expect the spectrophotometer pen to give a reading of $E_K + E'_{Rb}$ mm. In actual fact one always gets a reading $S_K > E_K + E'_{Rb}$. The difference $\Delta S = S_K - (E_K + E'_{Rb})$ demonstrates a deviation from additivity (Fig. 2). It should be observed that the background of the flame on its own (that is when the atomizer is not in operation) in the spectral region considered is vanishingly small [4]. The background caused by the main element of the sample was taken into account in the value E'_{Rb}. The deviation from additivity for the intensity of the components of the test solution is caused, as is well-known, by a number of factors which we shall not consider here (by the ionization and displacement of the ionization equilibrium, widening of the spectral lines, determined by the concurrent action of collison and the Doppler effect, etc.).

It follows from Fig. 2 that the region in which this deviation from additivity is observed (the region of the greatest mutual influence) lies at concentrations of 0.005-0.01% potassium. Accordingly, in order to develop a method of determining potassium in rubidium chloride, the original concentrations of potassium present as an impurity were chosen as 0.005-0.01%, for a concentration of the main element in the sample of 4 g/100 ml. This enabled us to avoid the use of too-large inlet and outlet slits. Higher concentrations of the main element led to difficulties in the operation of the atomizer.

In Fig. 3 are shown two calibration lines 1 and 2, constructed on a logarithmic scale from the results of Table 1. These two calibration lines correspond to different settings of the spectrophotometer (slits, air and acetylene pressure). Using these two lines 1 and 2, the same synthetic mixture (sample A) containing 0.0054% potassium was analyzed several times. The mean square arithmetical error was ± 0.0002, while the experimental error was − 3.7% (relative).

Bearing in mind the comparative complexity of preparing rubidium chloride standards with low potassium contents, we checked on the possibility of using one standard in the flame photometric method. For this purpose the potentiograms of the standard and of the sample were recorded, the mean value of I_K/I_{Rb} was calculated for the standard, and a point marked out on the calibration curve on the basis of the value obtained. Through the point thus obtained was drawn a new calibration curve parallel to the previous calibration curve.

Results of the analysis of sample A by this technique are given in Table 2. Each standard (sample) was measured photometrically at least three times. The mean arithmetic values of the potentiogram ordinate were taken for calculation. The mean square arithmetic error of the potentiogram ordinate did not exceed ± 5.5 mm, while the deviation of the results of individual measurements from their arithmetic mean did not exceed the mean error of a separate measurement by more than twice. The mean square arithmetic error of the analytical results obtained on using the one-standard method amounted to ± 0.00041 for a concentration of 0.0054% of the impurity to be determined. Our observations showed that in most cases, large errors are connected with the operation of the atomizer and the way in which it is fed, but are completely independent of the potentiometer.

A study was also made of the effect on the experimental accuracy of sodium, cesium, calcium, and magnesium chlorides, which are usually present as impurities in technical rubidium chloride.

It is clear from Table 3 that for the indicated amounts of potassium in rubidium chloride, the impurities listed above (with the exception of magnesium) have almost no effect on the accuracy of the determination when they are present in the sample in amounts up to 0.5%. Higher concentrations of these impurities in the sample affect the normal operation of the atomizer as a result of the increase in the viscosity of the solution being sprayed. Magnesium in amounts greater than 0.1% causes a decrease in the emission of potassium, when the concentration of the latter is 0.01%; this confirms published results.

Determination of rubidium in potassium chloride does not differ in any way from the determination of potassium in rubidium chloride.

SUMMARY

A flame photometric method has been developed for the determination of potassium present as an impurity in rubidium chloride, by means of an ISP-51 spectrograph coupled with a FÉP-1 photoelectric setup. The method recommended permits the development of a general scheme for the determination of certain alkali metals present as impurities in the water-soluble salts of other alkali metals.

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GRAVIMETRIC DETERMINATION OF SMALL AMOUNTS OF BERYLLIUM IN ORES AND IN PRODUCTS OBTAINED DURING THEIR TREATMENT

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For the analysis of materials with a high beryllium content either the gravimetric complexono-phosphate method [1], or the iodometric titrimetric method [2] are usually used. The photometric beryllon method is used for the determination of microgram amounts [3]. These methods, however, do not always ensure sufficiently high accuracy for the analysis of ore materials with beryllium contents ranging from 0.1 to 2-3%. A number of methods have been suggested for the determination of such amounts of beryllium in pure solutions; they include: the method of Benedetti-Pichler [4], in which beryllium sulfate is used as the gravimetric form; the method of Dutta and Sen Gupta [5] which consists of precipitating and weighing $BaBeF_4$, and also other methods of precipitating beryllium in the form of a complex compound with quinaldine [6], and in the form of $[Co(NH_3)_6]\cdot[(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$ [7]. There is no published information on the use of these methods for the determination of beryllium in ores.

In a previous communication [8] it was shown that 2,2-dimethylhexanedione-3,5 can be used for the quantitative determination of beryllium in solutions of its pure salts. This reagent forms a sparingly soluble complex compound with beryllium.

The present article is devoted to a description of a method for the determination of beryllium by means of the diketone indicated, in ores and in their processed products.

2,2-Dimethylhexanedione-3,5 was synthesized as described previously [9]. An aqueous solution of the diketone saturated with the latter at room temperature was used as the precipitant, the solution was prepared 2-3 days prior to use in order to give time for a keto-enol equilibrium to be established. Since the diketone indicated is not a sufficiently selective reagent for beryllium, sodium ethylenediaminetetracetate (EDTA-Na) was used as a masking agent.

Even a considerable excess of EDTA-Na has no effect on the completeness of precipitation of beryllium from aqueous solutions (Table 1).

A solution of ammonia can be used instead of pyridine for establishing the requisite pH in the presence of EDTA-Na. In this case the optimum pH range for precipitation is 7-8, while the amount of the saturated solution of the reagent required for precipitating 1 mg of beryllium is 15-20 ml.

Table 2 contains results for the determination of beryllium in the presence of the elements which accompany it most often; they include: aluminum, iron, calcium, and also the rare earths, UO_2^{2+} and Ti^{4+}.

As is evident, none of the elements indicated interfere with the determination of beryllium. Tin, which under the conditions used for precipitating beryllium does not form such stable compounds with EDTA-Na, interferes. Tin, however, only rarely accompanies beryllium. In most beryllium ores the elements which interfere with its determination by the suggested method, are absent. Phosphate ions do not interfere even at a

TABLE 1

Determination of Beryllium in the Presence of EDTA-Na (2.04 mg Be taken)

Molar ratio [Be]:[EDTA-Na]	Be found, mg	Molar ratio [Be]:[EDTA-Na]	Be found, mg
1:1	2,02	1:8	2,02
1:2	2,04	1:10	2,03
1:4	2,04	1:20	2,03
1:6	2,05	1:30	2,03

TABLE 2

Determination of Beryllium in the Presence of Foreign Elements

Be taken, mg	Foreign element	Amount of foreign element, mg	Be found, mg	Be taken, mg	Foreign element	Amount of foreign element, mg	Be found, mg
2,11	Fe^{3+}	200	2,11	1,02	Ca^{2+}	10	1,01
		200	2,10			20	1,01
2,11	Al^{3+}	600	2,11			30	1,02
		600	2,13	1,02	Ti^{4+}	10	1,02 1,02
2,04	Ce^{3+}	10	2,04			20	1,01 1,01
		20	2,03	1,02	UO_2^{2+}	10	1,02
2,04	Nd^{3+}	10	2,04			20	1,01
		20	2,03			30	1,02

TABLE 3

Determination of Beryllium in Ores

Sample wt., g	Be content found by the suggested method, %	Mean Be content, %	Be found, %		Sample wt., g	Be content found by the suggested method, %	Mean Be content, %	Be found, %	
			by the complexono-phosphate method	by the radio-activation method				by the complexono-phosphate method	by the radio-activation method
1,0	0,0461; 0,0475; 0,0454	0,0465	0,0483	0,050	1,0	0,0972; 0,0961; 0,0965	0,0972	0,0846	0,972
0,25	0,233; 0,234; 0,232	0,233	—	0,240	1,0	0,0727; 0,0720; 0,0720	0,0722	0,0727	0,0802
0,25	0,487; 0,483; 0,476	0,482	—	0,482	0,25	0,483; 0,482	0,482	—	0,500
0,5	0,156; 0,150; 0,150	0,152	—	0,159	0,5	0,139; 0,137; 0,136	0,136	—	0,122

molar ratio of Be: PO_4 of 1: 100; fluoride ions only start to interfere at a molar ratio of Be: F = 1: 20, while carbonate ions start interfering at 1: 30. SO_4^{2-}, Cl^-, NO_3^-, CH_3COO^- do not interfere with the determination.

Determination of beryllium in ores reduces to the following. 0.25-1.0 g of material (depending on the expected beryllium content) is fused in a platinum basin with five times its amount of potassium bifluoride in a muffle furnace at 800-900°. The melt is treated with 15 ml of H_2SO_4 1: 1, and the solution is evaporated until fumes of sulfuric acid cease to be evolved.

The contents of the basin are transferred to a 400 ml beaker, 10 ml of HCl 1: 1 is added, and the volume of the solution made up to 100 ml, and then boiled until the salts have dissolved completely. Where necessary, the solution is filtered through a "white band" filter paper and cooled to room temperature.* 35-40 ml of a 5% solution of EDTA-Na is then added, and the pH of the solution adjusted to 7-8 with ammonia (using universal indicator); having withdrawn the glass rod from the beaker, diketone solution at the rate of 20-30 ml for each mg of beryllium expected to be present is added to the beaker. The solution is mixed by adding 15-20 ml of water to it.

On adding the reagent the solution becomes turbid, and, after 2-3 hours the precipitate collects into coarse, friable flocs on the bottom of the beaker, and the supernatant solution becomes completely clear. Needle-like crystals are visible under the microscope. The precipitate is then filtered through a No. 4 filter crucible, it is washed several times with cold distilled water and is finally dried to constant weight at 45-55°. During the latter stage care must be taken to ensure that the temperature does not exceed 70-75°, when the precipitate starts to volatilize.

Two 40 minute dryings are sufficient to bring the precipitate to constant weight. The conversion factor to beryllium is 0.03096.

The results obtained are given in Table 3.

The suggested method for the determination of beryllium has a number of real advantages over the complexono-phosphate method. The beryllium compound which corresponds strictly to the formula $Be(CH_3 - CO-$ $-CH = CO - C(CH_3)_3]_2$; can be prepared by carrying out the precipitation operation once; this cuts down the analysis time considerably. Beryllium is precipitated in the form of a crystalline precipitate, which is easy to wash and can be brought to constant weight at low temperatures. The small conversion factor to beryllium is also very favorable.

SUMMARY

A description is given of a new gravimetric method for the determination of beryllium in ores and in their processed products; beryllium is precipitated in the form of its compound with 2,2-dimethylhexanedione-3,5. Elements which are complexed by EDTA-Na (Fe, Al, UO_2^{2+}, Ti, Ce, Nd, and Ca) do not interfere with beryllium determination. PO_4 ions and appreciable amounts of F and CO_3 do not interfere either. Tin must be removed.

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* When the sample contains tin, the latter is removed by precipitating it with hydrogen sulfide in an acid medium.

** Original Russian pagination. See C. B. Translation.

SEPARATION OF STRONTIUM AND CALCIUM BY MEANS OF SODIUM ETHYLENEDIAMINETETRACETATE (EDTA-Na) DETERMINATION OF STRONTIUM IN APATITES

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In a previous paper [1] the possibility was demonstrated of separating strontium and calcium by precipitating strontium as its sulfate from complexon-containing solutions. On the basis of these results we have carried out a more detailed study of the conditions for precipitating strontium and calcium sulfates from solutions containing sodium ethylenediaminetetracetate (EDTA-Na) and developed a technique for the quantitative separation of these elements at various ratios of one element to the other. The work carried out showed that precipitation of strontium sulfate in the presence of EDTA-Na starts at a pH of about 6, and proceeds quantitatively at pH's lower than 5. Precipitation of calcium sulfate starts at pH's below 4. Separation of strontium and calcium can be achieved at pH 4-5. From solutions of strontium and calcium salts containing sufficient EDTA-Na to complex both elements, strontium is completely precipitated by ammonium sulfate at a pH of about 4.5, while calcium remains in solution.

The necessary condition for the complete separation of strontium is the presence of sufficiently large amounts of ammonium sulfate and moderate amounts of EDTA-Na in solution.

When the relative amounts of strontium are considerable, separation of strontium from calcium proceeds quite satisfactorily in an aqueous medium. When the calcium predominates, then the EDTA-Na content of the solution becomes too high for precipitation of the strontium, as a result of which some of the latter may remain in solution with calcium. In such cases, completeness of separation of strontium can be ensured by addition of ethanol.

Depending on the content and proportions of strontium and calcium, the following two variants are suggested for separating and determining strontium and calcium in their mixtures.

Separation of large amounts of strontium from calcium. The method described below is applicable to mixtures containing strontium and calcium in the proportion of 1 : 5 and higher.

The mixture of strontium and calcium oxides is dissolved in the minimum amount of dilute nitric (or hydrochloric) acid. To the solution containing not more than 150 mg of oxides is added EDTA-Na at the rate of 800 mg per 100 mg of the oxides, after which a few drops of methyl red is added as indicator and ammonia added until the solution is yellow in color. Ten ml of a 10% solution of ammonium sulfate is added and the total volume of the solution made up to 30-45 ml. To the heated solution is added dropwise dilute sulfuric acid to the appearance of a stable rose color (pH about 4.5) and the solution plus precipitate left for 20-30 min at 70-80°. After two hours the precipitate is filtered through a small dense filter and is washed 5-6 times with water containing a small amount of ammonium sulfate. Strontium is finally determined gravimetrically or titrimetrically. In the first case the precipitate is calcined at a dark-red heat and weighed as $SrSO_4$. For the titrimetric variant, the precipitate plus filter are transferred back again into the beaker and is dissolved in the cold in an ammoniacal solution of EDTA-Na. Excess of the EDTA-Na is titrated with magnesium chloride using acid chrome-blue or eriochrome black T—tropeoline 00 as indicator. The calcium content of the mixture is calculated by difference, or is determined gravimetrically after precipitation of calcium in the filtrate in the form of its oxalate [4].

TABLE 1

Separation of Strontium from Calcium in Aqueous Solution

Taken, mg		Sr found, mg	Error in the determination of Sr	
Sr	Ca		mg	%
20,4	10 1	20,6	+0,2	,0
20,4	20,2	20,1	−0,3	5
20,4	105,8	20,3	−0,1	0,5
10,2	100	9,4	−0,8	8
5,4	100	4,1	−1,3	24

Results for the determination of strontium and calcium by this variant are given in Table 1. Strontium was determined titrimetrically. As is evident from the results adduced, the relative error for the determination of strontium at ratios of Sr: Ca ranging from 2: 1 to 1: 5 is about 1%. At lower strontium ratios the error increases appreciably; in such cases it is accordingly necessary to use the second variant of the method.

Separation of small amounts of strontium from large amounts of calcium. This variant is applicable for strontium contents not less than 1 mg and not more than 200 mg calcium.

The calcium and strontium oxides are dissolved in the minimum amount of nitric (or hydrochloric) acid. To the solution containing not more than 100 mg of the oxides is added EDTA-Na at the rate of 800 mg per 100 mg of the oxides, after which a few drops of methyl red is added followed by ammonia until the solution is yellow in color. The volume of the solution is made up to 30 ml and dilute sulfuric acid added until a rose color is obtained. Ten ml of an acetate buffer with a pH of 4.5 is then added (250 ml of 98% acetic acid and 100 ml of concentrated ammonia per liter) this is followed by 10 ml of a 10% solution of ammonium sulfate and 10 ml of 96% ethanol. When strontium is present, a milky turbidity of strontium sulfate appears after 1-2 minutes, or immediately (depending on the amount of strontium). After 24 hours the precipitate which has separated out is filtered through a double "blue band" filter paper, it is washed 5-6 times with 50% alcohol containing a small amount of ammonium sulfate, and is finally calcined to a dark-red heat and weighed as $SrSO_4$.

When the amount of the oxides in solution exceeds 100 mg good results can be obtained by carrying out a reprecipitation, since in such cases there is a possibility that calcium may be partially precipitated. For this purpose, the sulfate residue, after weighing, is returned to the beaker and EDTA-Na added (5-10 mg per mg of residue), ammonia is added until its odor is clearly distinguishable. The solution is heated until the precipitate has dissolved, after which it is acidified with dilute sulfuric acid using methyl red as indicator, 5 ml of the acetate buffer and 5 ml of ammonium sulfate solution are finally added. The total volume of the solution is made up to 25 ml and an equal volume of alcohol added. After 24 hours the precipitate which has separated out is filtered off, and washed 5-6 times with 50% alcohol containing a small amount of ammonium sulfate; it is finally calcined at a dark-red heat and weighed as $SrSO_4$.

The calcium content of the mixture can be calculated by difference, or can be determined directly after precipitation of calcium from the filtrate in the form of its oxalate.

This variant was checked on synthetic mixtures for ratios of Sr: Ca ranging from 1: 100 to 2: 1, in which the absolute amounts of strontium varied from 20 to 1 mg. The experimental results obtained (Table 2) showed that even under the most unfavorable ratios of strontium and calcium (Sr: Ca from 1: 100 to 1: 20), the relative error for the determination of strontium does not exceed 10%. At higher strontium contents this error is usually about 1%.

The purity of the separated precipitates was checked spectrographically. It was found that on separating mixtures containing strontium and calcium in the proportion 1: 10, contamination of strontium sulfate by calcium is about 1%. Strontium was found in traces in the CaO residue.

Determination of strontium in apatites. Precipitation of $SrSO_4$ from solutions containing the complexon permits the possibility of a simple and rapid determination of strontium in apatites. In this case there is no need for a preliminary separation of total strontium and calcium. Direct precipitation of strontium sulfate in the presence of EDTA-Na enables it to be separated not only from calcium, but also from all the other elements present in apatite.

TABLE 2

Separation of Strontium from Calcium in an Aqueous-Alcoholic Medium

Taken, mg		Sr found, mg	Error in the determination of Sr		Ca found (gravimetrically), mg
Ca	Sr		mg	%	
1000	0.9	0.9	0	0	–
100	1.8	1.9	+0.1	+5.5	–
100	2.7	2.8	+0.1	+3.7	–
100	3.6	3.9	+0.3	+8.3	–
100	4.8	4.8	0	0	–
100	10.0	10.0	0	0	–
51.2	10.0	10.1	+0.1	+1.0	50.8
51.2	20.0	20.2	+0.2	+1.0	50.8
10.2	10.0	10.0	0	0	10.4
10.2	20.0	20.1	+0.1	+0.5	10.5

TABLE 3

Results of the Determination of Strontium in Apatites

Sample No.	Strontium content, %	
	by the chemical method	by a mass-spectrographic method
430a	8,27	8,26
203a	4,07	4,11
849a	2,28	2,20
338	4,72	4,71
220	2,28	2,25

0.2 g of apatite is dissolved in nitric acid and 10 ml of a 10% solution of EDTA-Na added, a few drops of methyl red is then added, followed by ammonia until the solution is yellow. The solution is carefully acidified until a rose color appears, when 10 ml of the acetate buffer with pH 4.5, and 10 ml of 10% ammonium sulfate solution are added. The total volume is made up to 50 ml, after which an equal volume of 96% ethanol is added. After 24 hours the precipitate which has separated out is filtered off, washed 5-6 times with 50% alcohol containing a small amount of ammonium sulfate; it is finally calcined at a dark-red heat and weighed as $SrSO_4$.

This method was checked by determining strontium in five samples of apatites. In order to control the results obtained, in parallel with its chemical determination, the strontium content of the mineral was also determined mass-spectrographically by the isotope dilution technique.

The determination was carried out as follows. 0.02 g of sample was dissolved in a few drops of nitric acid after which a known amount of indicator solution with the following isotopic composition was added: Sr^{84}– 57.1%, Sr^{86} – 7.6%, Sr^{87} – 3.9% and Sr^{88} – 31.4%. The solution was carefully mixed, and, after addition of EDTA-Na, the strontium was precipitated with ammonium sulfate at a pH of 4.5, and alcohol added. The isolated strontium was placed on the ribbon of the ionic source directly, in the form of its sulfate after dissolving it in concentrated sulfuric acid. The isotopic composition was determined on a MI-1305 mass-spectrometer by a technique adopted in the Dokembrya Geological Laboratory, Academy of Sciences, USSR [3]. The ratio Sr^{84}/Sr^{88} was measured. The strontium content of the sample taken was calculated by means of the formula:

$$X = \frac{Sr^{84}_{cm}(1,85 - K)}{K} \cdot 0,682,$$

where X is the strontium content of the sample; $Sr^{84}{}_{cm}$ is the Sr^{84} content of the aliquot of indicator taken; 1.85 is the Sr^{84}/Sr^{88} ratio in the indicator; and K is the ratio Sr^{84}/Sr^{88} in the mixture obtained.

Results of the chemical and mass-spectrographic determinations of strontium are compared in Table 3. The good agreement obtained shows that the value obtained by the chemical method gives the true strontium content of the sample, and is not the result of a compensation of errors.

SUMMARY

A method has been developed for the quantitative separation of strontium and calcium; it is based on precipitation of strontium as its sulfate in the presence of EDTA-Na at a pH of 4.5. The method has been checked on synthetic mixtures of strontium and calcium in which the ratios of the two elements Sr: Ca varied from 2:1 to 1:100, and in which the absolute amount of strontium varied from 1 to 20 mg.

A simple and rapid method has been developed for the determination of strontium in apatites, and it has been compared with a mass-spectrographic isotope dilution method.

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COMPLEXONOMETRIC DETERMINATION OF ALUMINUM WITH AN AMPEROMETRIC INDICATION OF THE TITRATION END POINT

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Direct complexonometric determination is possible for Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Bi^{3+}, Ni^{2+}, Co^{III}, Fe^{3+}, Mn^{2+}, some of the rare earths, Zr, and Th [1-5]. In addition, by back titration, or by some other indirect complexonometric method, it is also possible to determine a number of other metals (Al, Ga, Zr, Ag, Au, Pd, Pt, and Na). Several papers have been devoted to the complexonometric determination of aluminum, but only in one of them is there suggested a direct determination of aluminum [6] in an acid solution using pyrocatecholsulfonphthalein as an indicator; in the remaining papers various back-titration methods were used [7-11].

Complexonometric indicators have quite clearly expressed drawbacks. This, to a certain degree, limits the application of sodium ethylenediaminetetracetate (EDTA-Na), particularly during the determination of aluminum in various objects.

Physicochemical methods of indicating the end point (potentiometry, amperometry) without doubt considerably expand the possibilities of the use of EDTA-Na. However, as far as aluminum is concerned, these methods are not used sufficiently. The only method known is a determination of aluminum by a back-potentiometric titration [4]. Several methods have been published on the amperometric determination of aluminum using sodium fluoride and 8-hydroxyquinoline [12-14]. We have been unable, however, to find in the literature any references to the amperometric titration of aluminum using EDTA-Na.

Aluminum can be determined amperometrically by direct titration with EDTA-Na, which, as Usatenko and Vitkina [15, 16] have shown, gives an anodic diffusion wave on a rotating platinum microanode. It is more expedient to carry out a back titration of excess EDTA-Na with a ferric salt, which, as is known, also gives a diffusion current on a platinum microelectrode. As a first step in the development of a method for the amperometric titration of aluminum by means of EDTA-Na, we chose a back-titration technique.

EXPERIMENTAL

Amperometric titration was carried out on an ordinary setup with a rotating platinum electrode as an indicator, without applying an external emf. The reference electrode was a saturated calomel electrode connected to the titration vessel via an agar-agar bridge.

The electrode was rotated at a rate of 700 rpm. The type M 198/1 galvanometer used had a sensitivity of $1 \cdot 10^{-8}$ per scale division.

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* Deceased.

TABLE 1

Determination of Aluminum
(0.400 mg Al taken)

Al found, mg	Error	
	mg	%
0.406	0.006	1.5
0.409	0.009	2.25
0.400	–	–
0.403	0.003	0.75

Titration was carried out in 50 ml vessels.

The EDTA-Na solution was prepared by dissolving an aliquot and then standardizing the solution against $MgSO_4$.

The concentration of the ferric chloride solution was determined iodometrically.

Initially, conditions for determination of Al^{3+} in solutions of its pure salts were established. Experiments were carried out as follows. To 1 ml (titer – 0.004 g) of a standard solution of an aluminum salt, prepared by dissolving an accurately weighed aliquot of aluminum metal, was added 5 m of 0.1 M EDTA-Na solution; this was followed by 0.2 ml CH_3COONH_4 (50% solution) in order to adjust the pH to 5. The pH was controlled by universal indicator paper. The volume of the solution was made up to 25 ml with distilled water and was finally titrated with 0.1 M ferric chloride solution.

The results obtained (Table 1) show that aluminum can be determined fairly accurately in pure solutions, by amperometric titration with EDTA-Na.

There are published references to the fact that magnesium cations form a stable complex in an alkaline medium [4].

The logarithms of the instability constants [17] of magnesium, aluminum, and iron have the following values:

for magnesium ethylenediaminetetracetate		8.69;
for aluminum	"	16.13;
for iron	"	25.1

Only the most stable complexes are formed in acid solutions, this gives the possibility of titrating with a ferric salt not only the free acid EDTA, but also EDTA-Mg. We have checked on the possibility of determining aluminum in the presence of magnesium. During the determination of Al^{3+} in the presence of various amounts of Mg^{2+} at ratios of Al:Mg = 1:10, 1:12.5, completely accurate results were obtained in 16 experiments, the relative error was 0% even for the highest magnesium contents, while in four experiments it did not exceed 2.5%.

The presence of large amounts of magnesium does not interfere with aluminum determination. We have also established that the presence of small amounts of zinc does not affect the accuracy of aluminum determination.

For the determination of aluminum in alloys based on magnesium (88.8% Mg, 0.05% Fe) by the proposed method, an aliquot of 1 g is dissolved in 20 ml HCl (1:1), the solution is transferred to a 200 ml standard flask and its volume made up to the mark with distilled water. One ml of this solution is transferred to a 50 ml beaker, 2 ml of 0.1 M EDTA-Na and 0.2 ml of CH_3COONH_4 (50% solution) are added, and the volume made up to 25 ml with distilled water; the solution is finally titrated with 0.1 M ferric chloride.

The end point is found graphically. The aluminum content is calculated by means of the formula:

$$\frac{[v_1-(v_2a)]\,TP\cdot b\cdot 100}{v_k}\,\%\ \mathrm{Al},$$

where v_1 is the volume of EDTA-Na in ml; v_2 is the volume of ferric chloride in ml; a is the amount of EDTA-Na in ml corresponding to 1 ml of ferric chloride solution; T is the titer of EDTA-Na with respect to aluminum in g; P is the weight of alloy in mg; b is the amount in ml of the solution of the alloy taken for titration; and v_k is the volume of the flask in ml.

Results for the determination of aluminum in several samples of magnesium alloys by the method suggested, and by the GOST 3240-56 gravimetric method "Magnesium Alloys," are given in Table 2.

Other impurities in the alloys analyzed (0.25% Zn, and 0.05% each of Cu, Mn, Ni, and Fe) are contained in such small amounts that they show almost no effect on the determination of aluminum.

TABLE 2

Determination of Aluminum in Alloys

Alloy	Aluminum found by a gravimetric method	Aluminum found by the amperometric method	deviation, %
MA-331	7.67	7.88	0.21
MA-331	7.67	7.67	–
	7.67	7.77	0.10
MA-422	9.11	9.18	0.07
	9.11	9.32	0.21
	9.11	9.32	0.21
MA-904	7.91	8.10	0.19
	7.91	7.91	–
	7.91	8.01	0.10

TABLE 3

Tempometric Titration of Mixtures of Aluminum and Magnesium

Series	Expt. No.	Experiment time, sec	Mean time, sec	Aluminum taken, mg	Aluminum taken, ml	Amount of magnesium, mg	Amount of magnesium, ml
I	1	192,2	192,7	2	0,5	35,52	1
	2	192,6					
	3	192,8					
	4	193,2					
II	1	159,2	158,9	4	1	35,52	1
	2	159,2					
	3	158,4					
	4	158,8					
	5	159,0					
III	1	125	125,2	6	1,5	35,52	1
	2	125,6					
	3	125,2					
	4	125					
IV	1	94,2	95,2	8	2	35,52	1
	2	95,4					
	3	95,8					
	4	94,8					
	5	96,0					
V	1	61,0	60,6	10	2,5	35,52	1
	2	60,6					
	3	61,0					
	4	59,8					

An attempt was made to increase the accuracy and cut down the analysis time by the method proposed and by the GOST 3240-56 method "Magnesium Alloys" set forth and described in a number of papers [18, 19]. In the drop-tempometric method, the concentration of the test material is determined by means of a calibration curve, on whose abscissa time is plotted, while on the ordinate concentrations of standard solutions are plotted.

In Fig. 1 is shown a schematic diagram of a setup for the amperometric titration of aluminum by a drop-tempometric method without application of an external emf. The accuracy of tempometric titration depends to a considerable extent on the uniform supply of solution from the buret. For this purpose a tempometric buret (m) was adopted, this buret,which has a constant difference in the liquid levels (h), ensures an uniform supply of solution. The discharge rate was controlled by means of a capillary (k) and was equal to 10 drops in 11 sec.

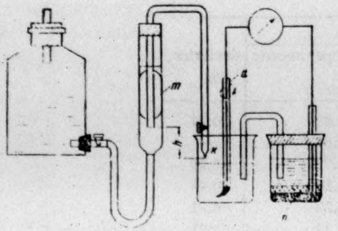

Fig. 1. m) Tempometric buret; k) capillary; a) rotating platinum electrode; n) saturated calomel electrode.

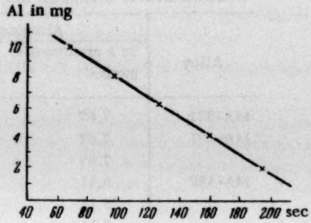

Fig. 2.

TABLE 4

Determination of Aluminum in Alloys

Alloy	Found, %		Deviation, %	Duration of titration, sec
	by a gravimetric method	by the tempometric method		
MA-422	9,11	9,14	+0,03	149,9
	9,11	9,11	—	150;4
	9,11	9,01	—0,10	151,0
	9,11	9,07	—0,04	150,8
	9,11	9,13	+0,02	150,0
MA-331	7,67	7,65	—0,02	161,8
	7,67	7,71	+0,04	161,4
	7,67	7,67	—	162,0
	7,67	7,72	+0,05	161,2
	7,67	7,59	—0,08	162,6
MA-904	7,91	7,80	—0,011	161,0
	7,91	7,90	—0,001	160,6
	7,91	7,80	—0,11	161,0
	7,91	7,86	—0,05	160,8

The order in which the tempometric method was carried out was as follows: the beaker containing the test solution was placed in the apparatus and the rotating platinum electrode switched on. At the same time the tap of the tempometric buret was opened and a stopwatch started. Titration was regarded as complete when the galvanometer needle started to shift rapidly from its original position. At this point the stopwatch was switched off and the tap of the tempometric buret turned off. The concentration of the test solution was determined from a calibration curve of "time against concentration of standard solution."

The standard solution was prepared so that the same amount of magnesium (35, 52 mg) was contained in the volume to be titrated, while the amount of aluminum was changed (2, 4, 6, 8, 10 mg). The results obtained are given in Table 3.

A calibration curve was constructed from the results obtained by the titration of a standard mixture (Fig. 2). The aluminum content of magnesium alloys was determined by means of this curve (Table 4).

The sample was dissolved and prepared for analysis by the same method as that used for the amperometric titration.

The second variant of determining aluminum in magnesium alloys gives the most accurate results, while an analysis is carried out in half the time taken for the first variant. The analysis time is cut down by using

the semiautomatic method of supplying the solution, and by determining the end point during continuous titration visually, by following the galvanometer needle. In the titration of two parallel samples in which the volume was measured the time taken was 30-35 min, while by the tempometric method the time taken was 3.5 min.

Taking into account that the method of preparing the alloy for analysis is the same in both variants, the saving in time obtained is determined solely by the improved method of titration.

The time taken to determine aluminum in magnesium alloys, including decomposition of the sample, is 30 min. Thus, the drop-tempometric method of determining aluminum by the proposed method is an express method.

SUMMARY

An amperometric method is suggested for the determination of aluminum in magnesium alloys by means of EDTA-Na, without removing the aluminum from the other components. The experimental accuracy is about 0.2% (absolute).

On the basis of the method suggested a rapid and accurate tempometric method of determining aluminum in magnesium alloys has been developed.

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RESEARCH IN THE ANALYTICAL CHEMISTRY OF THALLIUM

COMMUNICATION 5. A STUDY OF COMPLEXONOMETRIC INDICATORS FOR TRIVALENT THALLIUM*

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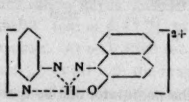
Comparatively few color reactions are known for trivalent thallium ions. Chromotropic azo dyes, for example, give a color effect with thallium [1]. There are almost no indicators for the complexonometric determination of thallium at low pH values when the selectivity of the method is comparatively high. Of interest, accordingly, was a study of the interaction of trivalent thallium at pH 2 with a complexonometric indicator recently suggested [2], namely 1-(2-pyridylazo)-2-naphthol, and also with 1-(2-pyridylazo)-resorcinol, and xylenol orange (the latter has been used by Kinnunen and Wennerstrand [3] for titrating thallium at pH 4-5).

The aim of our work was to determine the equilibrium constant and the optical characteristics of the reagents employed, and of the compounds formed by them with trivalent thallium, in order to choose the optimum conditions for their use as complexonometric indicators.

1. The interaction of trivalent thallium with 1-(2-pyridylazo)-2-naphthol. A $5.816 \cdot 10^{-4}$ M solution of the reagent in methanol was used in the work; it was prepared by dissolving an accurately weighed amount of the preparation synthesized by Chichibabin's method [4]; its m. p. was 138°.

1-(2-Pyridylazo)-2-naphthol forms with trivalent thallium a red-violet-colored compound which is rather sparingly soluble in water; its solubility increases in the presence of organic solvents which are miscible with water such as methanol, ethanol, and acetone. The best solvents of those which are immiscible with water are the higher alcohols and carbon tetrachloride.

The light-absorption curves taken on a SF-4 spectrophotometer with an incandescent lamp show that at pH 4.5 solutions of 1-(2-pyridylazo)-2-naphthol have a maximum light absorption at 470 mμ; this maximum, on addition of a trivalent thallium salt, shifts to 560 mμ (Fig. 1). Using the method of isomolar series (for a total molar concentration of $1.163 \cdot 10^{-4}$ M, and pH of 2.2) it was established that thallium and 1-(2-pyridylazo)-2-naphthol react in a molar ratio of 1:1 (Fig. 2). Taking into account that in dilute solutions multinuclear complexes are not formed, it can be assumed that formation of a complex cation occurs:



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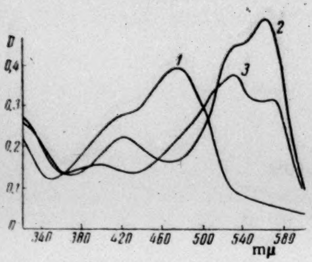


Fig. 1. Light-absorption curves of a $2.33 \cdot 10^{-5}$ M solution of 1-(2-pyridylazo)-2-naphthol: 1) at a pH of 4.5; 2) in the presence of tenfold molar excess of Tl^{3+} salt at pH 4.5; 3) in 0.1 M NaOH; l = 1 cm.

TABLE 1

Relation between Cl/D and the Compound of Thallium with 1-(2-Pyridylazo)-2-naphthol

C, M	D	Cl/D	$1/\sqrt{D}$
$5,82 \cdot 10^{-5}$	1,92	$6,1 \cdot 10^{-5}$	0,72
$4,65 \cdot 10^{-5}$	1,40	$6,6 \cdot 10^{-5}$	0,84
$3,49 \cdot 10^{-5}$	0,92	$7,6 \cdot 10^{-5}$	0,04
$2,91 \cdot 10^{-5}$	0,71	$8,2 \cdot 10^{-5}$	1,19
$2,33 \cdot 10^{-5}$	0,475	$9,8 \cdot 10^{-5}$	1,45
$1,74 \cdot 10^{-5}$	0,280	$12,4 \cdot 10^{-5}$	1,89
$1,16 \cdot 10^{-5}$	0,175	$13,3 \cdot 10^{-5}$	2,39

In order to determine the equilibrium constant of the complex formation reaction of trivalent thallium with 1-(2-pyridylazo)-2-naphthol, and the molar light absorption coefficient of the compound thereby formed, the method of Komar' as modified by Tolmachev [5] was used; Tolmachev's modification consists of interpreting the results graphically. The experimental method reduces to measuring the light absorption at 560 mμ of a series of colored solutions of varying concentration, in which the ratio of the concentration of the metal ion to the concentration of the addendum was kept constant and equal to 1 : 1 in accordance with the molar ratio established. All the solutions contained 50% (by volume) of methanol in order to increase the solubility of the thallium compound; the hydrogen ion concentration was kept constant by means of a buffer solution with a pH of 2.2 prepared from 0.1 M $KHC_8H_5O_6$ and 0.1 M $HClO_4$. The temperature of the test solutions was 20 ± 1°. The layer thickness of the cuvette was l = 1.997 cm. The results obtained are given in Table 1.

The straight line within the coordinates Cl/D – ($1/\sqrt{D}$) has a slope of $5.48 \cdot 10^{-5}$ and cuts a segment $4.6 \cdot 10^{-5}$ on the ordinate, which is numerically equal to the reciprocal of the true molar coefficient of light absorption. From this:

$$\varepsilon = \frac{1}{4,6 \cdot 10^{-5}} = 2,17 \cdot 10^{4}.$$

The equilibrium constant will be:

$$K = \frac{10^{-2,2} \cdot 1,997}{2,17 \cdot 10^{4}\,(5,48 \cdot 10^{-5})^{2}} = 1,93 \cdot 10^{2}.$$

Knowing the values of the equilibrium constant, it is possible to determine the stability of the complex as a function of the pH. 1-(2-Pyridylazo)-2-naphthol is a very weak acid; cleavage of the proton from the hydroxy group, which is accompanied by a color change from yellow to red-violet, starts at pH > 11. The concentration of free R^- ions depends essentially on the pH, in the same way that the stability of the complex with thallium also depends on the pH. $K'_{stab} = K_{stab} / a_H$ where $a_H = 1 + [H^+]/K_{HR}$:

$$K_{stab} = \frac{[TlR^{2+}]}{[Tl^{3+}][R^-]} = \frac{[TlR^{2+}][H^+]}{[Tl^{3+}][HR] \cdot K_{HR}} = \frac{equil}{K_{HR}};$$

$$K'_{stab} = \frac{K_{equil}}{K_{HR}\left(1 + \dfrac{[H^+]}{K_{HR}}\right)}; \quad K'_{stab} = \frac{K_{equil}}{K_{HR} + [H^+]}.$$

When $[H^+] \gg K_{HR}$, then the value of K_{HR} in the numerator can be ignored. We then get

$$K'_{stab} = \frac{K_{equil}}{[H^+]}.$$

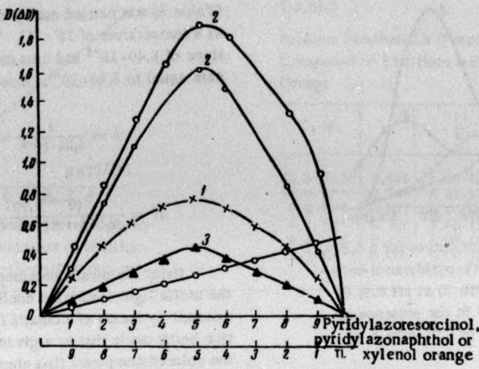


Fig. 2. Curve of "composition against optical density" for the systems: 1) Tl^{3+} – 1-(2-pyridylazo)-2-naphthol; 2) Tl^{3+} – 1-(2-pyridylazo)-resorcinol; 3) Tl^{3+} – xylenol orange.

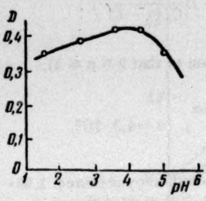


Fig. 3. Relation between pH and the optical density of a solution of the compound of thallium with 1-(2-pyridylazo)-2-naphthol.

The compound formed is not particularly stable at low pH values. The color of the complex increases with increasing pH, and decreases in the region where the trivalent thallium ion hydrolyzes (Fig. 3). Chloride and bromide ions affect the color of the complex strongly, and, in the presence of the latter at pH 1-2, the complex of thallium with 1-(2-pyridylazo)-2-naphthol changes over completely into bromide complexes as soon as a 2-3-fold molar excess of bromide ions is added. Photometric determination of thallium by means of 1-(2-pyridylazo)-2-naphthol is not of practical significance on account of its low selectivity at pH 4-5, and because of the limited solubility of the compound formed.

2. Interaction of trivalent thallium with 1-(2-pyridylazo)-2-resorcinol. A $5.816 \cdot 10^{-4}$ M solution of 1-(2-pyridylazo)-resorcinol was used in this work; this was prepared by dissolving an accurately weighed amount of the base synthesized by Chichibabin's method [6] and having a m. p. of 185-186° in water, and alkalizing the solution.

1-(2-Pyridylazo)-resorcinol reacts with trivalent thallium to form a red-colored compound which is fairly soluble in water, butanol, and isoamyl alcohol, but is insoluble in diethyl ether, benzene, carbon tetrachloride, and chloroform. The reagent is a dibasic acid. The first proton splits off in an acid medium, and the second one in a strongly alkaline medium (starting at pH 11). Actually, the light-absorption curves of a solution of the reagent at pH 1.5 and 5.0-5.5 differ from each other; this is obviously connected with the presence of undissociated molecules (H_2R) in equilibrium with HR^- ions at pH 1.5. In the pH range 3-11 almost only HR^- ions with a maximum light absorption at 415 mμ exist. At pH 13 the second proton starts to split off with formation of R^{2-} ions (maximum light absorption 495 mμ). At pH 2.2, the reagent, in the presence of a tenfold molar excess of trivalent thallium salt, has a maximum light absorption at 520 mμ (Fig. 4). The curve "composition – – optical density," and also the curve "composition – difference in optical density of the solution and the optical density of the colored reagent," at a constant total molar concentration of the reactants have a maximum at a molar ratio of the components of 1 : 1 (Fig. 2).

Determination of the equilibrium constant of the reaction of complex formation between trivalent thallium and 1-(2-pyridylazo)-resorcinol, and of the molar light-absorption coefficient of the compound formed

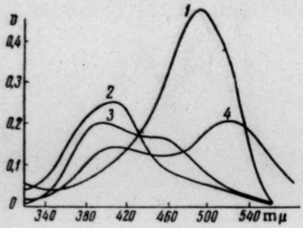


Fig. 4. Light-absorption curves for a $5.81 \cdot 10^{-6}$ M solution of 1-(2-pyridylazo)-resorcinol: 1) in 0.1 M NaOH; 2) at pH 5.5; 3) at pH 1.5; 4) at pH 2.2 in the presence of a tenfold molar excess of Tl^{3+} salt; l = = 1.997 cm.

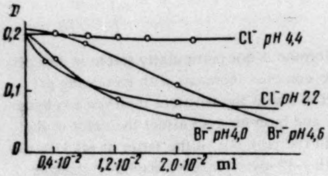


Fig. 5. Relation between the optical density of a $1.16 \cdot 10^{-5}$ M solution of the compound of Tl^{3+} with 1-(2-pyridylazo)-resorcinol and the concentration of halogen ions.

TABLE 2

Determination of the True Molar Extinction Coefficient of the Compound Formed Between Trivalent Thallium and 1-(2-Pyridylazo)-resorcinol

C, M	D	Cl/D	$1/\sqrt{D}$
$3{,}49 \cdot 10^{-5}$	1,20	$5{,}81 \cdot 10^{-5}$	0,91
$2{,}33 \cdot 10^{-5}$	0,78	$5{,}96 \cdot 10^{-5}$	1,13
$1{,}74 \cdot 10^{-5}$	0,57	$6{,}07 \cdot 10^{-5}$	1,32
$1{,}40 \cdot 10^{-5}$	0,46	$6{,}12 \cdot 10^{-5}$	1,47
$1{,}16 \cdot 10^{-5}$	0,37	$6{,}29 \cdot 10^{-5}$	1,64
$9{,}31 \cdot 10^{-6}$	0,29	$6{,}41 \cdot 10^{-5}$	1,86
$6{,}98 \cdot 10^{-6}$	0,21	$6{,}64 \cdot 10^{-5}$	2,18

(Table 2) was carried out by the method indicated above at a temperature of 15 ± 1°. The straight line has a slope of $6.40 \cdot 10^{-6}$ and cuts out a segment on the ordinate equal to $5.54 \cdot 10^{-5}$. Accordingly,

$$\varepsilon = \frac{1}{5{,}54 \cdot 10^{-5}} = 1{,}805 \cdot 10^{4},$$

$$K = \frac{10^{-2{,}2} 1{,}997}{1{,}805 \cdot 10^{4} (6{,}40 \cdot 10^{-6})^{2}} = 1{,}70 \cdot 10^{4}.$$

Using the results obtained (Table 2), we calculated the molar light-absorption coefficient and the equilibrium constant by means of Komar's formulas [7], the assumption being made that at a given wavelength it is not only the colored compound that absorbs but also the reagent itself. The molar extinction coefficient of the acid form of the reagent is $4.3 \cdot 10^{3}$. The molar coefficient of the compound formed was calculated by means of the formula:

$$\varepsilon_x = \frac{1}{l} \left(\frac{D_i}{C_i} + B \frac{D_i - n D_k}{C_i (n - B)} \right),$$

where $n = C_i / C_k$ (it was chosen so that $2 \leq n \leq 5$),

$$B = \left(\frac{D_i - \varepsilon l C_i}{D_k - \varepsilon l C_k} \right)^{1/2}, \quad \varepsilon = 4{,}3 \cdot 10^{3}.$$

The following values of ϵ_x were thereby obtained: $1.93 \cdot 10^4$; $1.95 \cdot 10^4$; $1.85 \cdot 10^4$; $1.91 \cdot 10^4$; $2.07 \cdot 10^4$, a mean value of $1.94 \cdot 10^4$. The value of the constant was calculated by means of the formula:

$$\frac{D_i - \varepsilon l C_i}{l (\varepsilon_x - \varepsilon)} = \frac{1}{h} K \left(\frac{C_i l \varepsilon_x - D_i}{l (\varepsilon_x - \varepsilon)} \right)^{2}$$

where $\underline{h}$ is the hydrogen ion concentration. The following values of K were obtained: $0.76 \cdot 10^4$; $0.77 \cdot 10^4$; $0.80 \cdot 10^4$; $0.63 \cdot 10^4$; $1.01 \cdot 10^4$; $0.81 \cdot 10^4$; $0.79 \cdot 10^4$, a mean value of $0.80 \cdot 10^4$, i.e., almost half the value obtained graphically without taking into account absorption by the reagent itself at 520 mμ.

In accordance with the greater stability of the complex of trivalent thallium with 1-(2-pyridylazo)-resorcinol, the effect of chloride and bromide ions on its color is not so markedly expressed, particularly at high pH values (Fig. 5). The relation between the color and the pH is similar to that for the compound of thallium with 1-(2-pyridylazo)-2-naphthol (see Fig. 3).

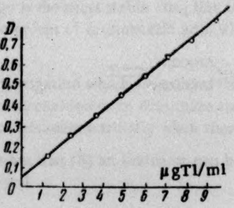


Fig. 6. Calibration curve for photometric determination of thallium by means of 1-(2-pyridylazo)-resorcinol at 520 mμ.

TABLE 3

Relation Between Cl/D and DY_2 for the Compound of Thallium with Xylenol Orange

C, M	D	$\frac{Cl}{D}$	$\frac{1}{\sqrt{D}}$
$13{,}3 \cdot 10^{-6}$	0,445	$5{,}98 \cdot 10^{-5}$	1,50
$11{,}0 \cdot 10^{-6}$	0,348	$6{,}31 \cdot 10^{-5}$	1,69
$8{,}9 \cdot 10^{-6}$	0,277	$6{,}40 \cdot 10^{-5}$	1,90
$6{,}7 \cdot 10^{-6}$	0,206	$6{,}46 \cdot 10^{-5}$	2,20
$4{,}4 \cdot 10^{-6}$	0,127	$6{,}98 \cdot 10^{-5}$	2,80
$2{,}2 \cdot 10^{-6}$	0,055	$8{,}06 \cdot 10^{-5}$	4,26

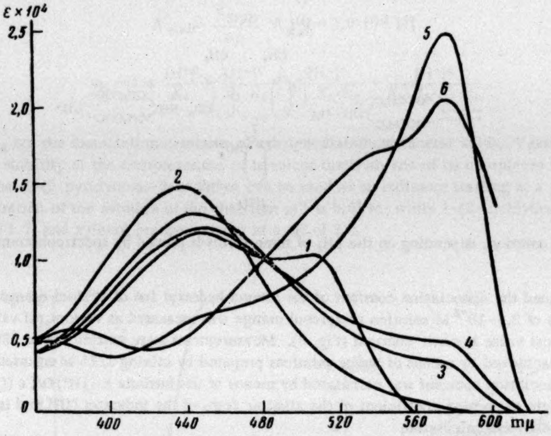
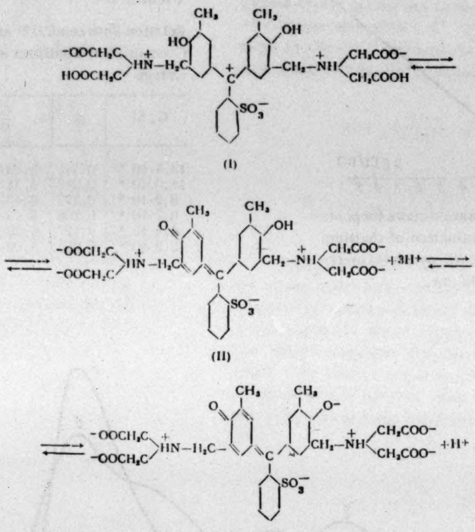


Fig. 7. Light-absorption curves of xylenol orange at various pH values: 1) in 1 M $HClO_4$; 2) at a pH of 3,6; 3) at a pH of 5.4; 4) at a pH of 6,0; 5) at a pH of 8,2; 6) in the presence of a tenfold molar excess of Tl^{3+} salt at pH 5,0.

Colored solutions containing the compound formed between trivalent thallium and 1-(2-pyridylazo)-resorcinol conform to Beer's law over the concentration range 1-10 μg Tl/ml (the optical density was measured at 520 mμ in a cuvette with a layer thickness of 1 cm, the blank solution was water) (Fig. 6).

3. Interaction of trivalent thallium with xylenol orange. Xylenol orange supplied by the "Khemapol" firm was used in the work. The indicator is a sexibasic acid (H_6R). In strongly acid solutions it has a rose color and is present in solution in the form of H_6R (I); at pH > 2 the rose color changes to yellow, which is obviously connected with the formation of H_3R^{3-} ions (II). This is accompanied by the splitting off of a proton from one of the OH-groups located in the para position with respect to the central carbon atom (in this pH range, presumably, splitting of protons from two carboxyl groups occurs). At pH > 6 a red-violet color appears which is determined by the change of the indicator into the H_2R^{4-} (III) alkali form. The hydrogen ions in the imino groups possess very weakly expressed acid properties and only split off in a strongly alkaline medium (pH about 11).



(I)

(II)

(III)

The existence in solution, depending on the pH, of three forms is proved by spectrophotometric measurements (Fig. 7).

We have determined the dissociation constant of the second hydroxyl ion of xylenol orange; for this purpose the optical density of $2.0\cdot10^{-5}$ M solution of xylenol orange was measured at various pH values up to the point at which the optical value became constant (Fig. 8). Measurements were carried out at 580 mμ. The requisite pH value was achieved by means of buffer solutions prepared by mixing 1/15 M solutions of Na_2HPO_4 and NaH_2PO_4. The dissociation constant was calculated by means of the formula $K=[H^+]D/[\epsilon([H_6R]_{total}]-D/\epsilon)$ where ϵ is the molar light extinction coefficient of the alkaline form of the indicator (III) and is equal to 28,000. The dissociation constants were calculated:

pH	7,25	7,45	7,70	7,90	8,08	8,50
K	$2,6\cdot10^{-8}$	$2,74\cdot10^{-8}$	$1,93\cdot10^{-8}$	$2,15\cdot10^{-8}$	$3,24\cdot10^{-8}$	$2,32\cdot11^{-8}$

The mean value of $pK_{diss} = 7.6$. From the pH value at which $D = 1/2D_M$, the value $pK_{diss} = 7.7$ (Fig. 8) was determined graphically.

The light-absorption curve of the compound of trivalent thallium with xylenol orange has a maximum at 580 mμ. Using the isomolar-series method for a total molar concentration of $4.44\cdot10^{-5}$ M and a constant pH of 2.5, it was shown that trivalent thallium and xylenol orange react in the molar ratio of 1:1 (Fig. 2).

Determination of the equilibrium constant was carried out at pH 1.4 in a series of solutions with varying metal concentrations (Table 3).

The straight line within the coordinates $Cl/D - 1/\sqrt{D}$ has a slope of $7.34\cdot10^{-6}$ and intersects the ordinate to give a segment equal to $5.0\cdot10^{-5}$. Accordingly, $\epsilon = 2.00\cdot10^{-4}$, while $K = (10^{1.4}\cdot5.0\cdot10^{-5}\cdot1.997)/(7.34\cdot10^{-6})^2 = 7.39\cdot10^4$. In parallel, measurements of the optical density of another series of solutions in a cuvette with a layer thickness of 1 cm gave the following results:

$$\epsilon = 1{,}96\cdot10^4 \text{ and } K = \frac{10^{-1{,}4}\cdot5{,}1\cdot10^{-5}}{(5{,}04\cdot10^{-6})^2} = 8{,}00\cdot10^4.$$

the mean value $K_{mean} = 7.7 \cdot 10^4$, and $\epsilon = 1.98 \cdot 10^4$. It is easy to see that the compound of thallium with xylenol orange is the most stable one; this can be explained by the presence in the molecule, apart from OH groups, of two groups of iminoacetic acid which possess a high complexing capacity with respect to multivalent ions.

The investigation which we carried out on the stability of the complexes of thallium with the indicators indicated above, enabled us to determine the minimum permissible pH value at which trivalent thallium can be titrated complexonometrically when these indicators are used.

It is known that [8] an indicator can be used for complexonometric titration as long as the following conditions is obeyed:

$$pC_0 + 2 \leqslant \log K''_{stab} \leqslant \log K'_{stab} - 2,$$

where C_0 is the initial concentration of the solution being titrated, K'_{stab} is the "apparent" stability constant of the complexonate at a given pH value, and K''_{stab} is the "apparent" stability constant of the complex of thallium with the indicator at the same pH value.

$$K'_{stab} = \frac{K_{stab}}{a_H}; \; K_{stab} = 2{,}9 \cdot 10^{23} \; [9]$$

$$a_H = 1 + \frac{[H^+]}{K_4} + \frac{[H^+]^2}{K_3 \cdot K_4} + \frac{[H^+]^3}{K_2 \cdot K_3 \cdot K_4} + \frac{[H^+]^4}{K_1 \cdot K_2 \cdot K_3 \cdot K_4} \quad (9)^{*}$$

(K_1, K_2, K_3, and K_4 are the dissociation constants of ethylenediaminetetracetic acid). Taking into account the dependence of the stability of the complexonate of trivalent thallium and of its complexes with indicators (Fig. 9) on pH, we found that 1-(2-pyridylazo)-2-naphthol can be used as an indicator starting at a pH of 1.8, as long as the initial concentration of the solution of the thallium salt is 0.01 M, while 1-(2-pyridylazo)-resorcinol can be used starting at pH 1.7, and xylenol orange starting at a pH of 2.0.

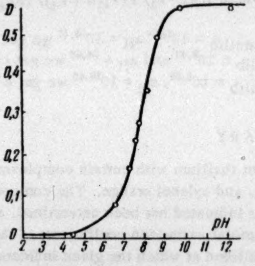


Fig. 8.

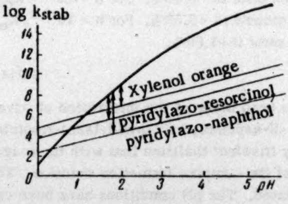


Fig. 9.

Fig. 8. Relation between the optical density of xylenol orange and pH.

Fig. 9. Stability as a function of pH: 1) complexonate of trivalent thallium; 2) the complex of thallium with xylenol orange; 3) the complex of thallium with 1-(2-pyridylazo)-resorcinol; 4) the complex of thallium with 1-(2-pyridylazo)-2-naphthol.

Experimental results are in good agreement with these conclusions. As shown earlier [2], 1-(2-pyridylazo)-2-naphthol can be used as an indicator starting from a pH of 1.8. At the same pH it is possible to use 1-(2-pyridylazo)-resorcinol and xylenol orange, their selectivity, however, is considerably lower than that of 1-(2-pyridylazo)-2-naphthol.

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* As in the Russian original.

Calculation of the theoretical errors arising during the complexonometric titration of thallium with the given indicators under the conditions indicated above shows that the titration error is − 0.45% when 1-(2-pyridylazo)-2-naphthol is used as indicator, +0.68% when 1-(2-pyridylazo)-resorcinol is used as indicator, and +1.88% when xylenol orange is used. The calculation reduces to a search for the complexon concentration(φ) which it is necessary to add to the solution of a trivalent thallium salt at a given pH value, in order that there should be a change in the color of the indicator (or, in other words, in order that the ratio of the concentration of the free indicator to the concentration of the indicator combined by the metal ion be 10: 1). The following equilibria occur in the system:

$$\mathrm{Tl^{3+} + H_2O \rightleftarrows TlOH^{2+} + H^+} \qquad pK_1 = 1{,}14$$

$$\mathrm{TlY^- \rightleftarrows Tl^{3+} + Y^{4-*}} \qquad pK_2 = 22{,}5$$

$$\mathrm{HTlY \rightleftarrows TlY^- + H^+} \qquad pK_3 = 2{,}3$$

$$\mathrm{Tl^{3+} + HR \rightleftarrows TlR^2 + H^+} \qquad K_{\text{equil.}} = \frac{[\mathrm{TlR^{2+}}][\mathrm{H^+}]}{[\mathrm{Tl^{3+}}][\mathrm{HR}].}$$

Introducing the designations $[\mathrm{Tl^{3+}}] = x$, $[\mathrm{TlOH^{2+}}] = y$, $[\mathrm{TlY^-}] = z$, $[\mathrm{HTlY}] = u$, $[\mathrm{TlR^{2+}}] = v$, $[\mathrm{Y^{4-}}] = s$, $[\mathrm{HR}] = w$, $[\mathrm{H^+}] = h$, we obtain:

$\varphi = z + u + s \cdot a_H$ (1) $\qquad K_1 x = yh$ (5)

$c = x + y + z + u + v$ (2) (c is the initial concentration of the solution being titrated) $\qquad K_2 z = xs$ (6)

$w = 10v$ (3) $\qquad K_3 u = zh$ (7)

$c_1 = w + v$ (4) (c_1 is the concentration of the indicator added) $\qquad K_p = \dfrac{h}{10x}$ (8).

From (1) and (2) we obtain: $c - \varphi = x + y + v - s \cdot a_H$ or $c - \varphi = (h/10K_{\text{equil.}}) + [K_1/(10K_{\text{equil.}})] + (C_1/11) - [(10K_2 \cdot K_{\text{equil.}} \cdot a_H)/h]z$; bearing in mind that $\varphi = z + (zh/K_3) + [(10K_2 \cdot K_{\text{equil.}} \cdot a_H)/h]\,z$, we have $c - \varphi = \{(h + K_1)/10K_{\text{equil.}} + (c_1/11) - (A \cdot B)/\,[1 + (h/K_3)\}$, where $A = c - c_1/11 - [(h + K_1)/10K_{\text{equil.}}]$, and $B = (10K_2 \cdot K_{\text{equil.}} \cdot a_H)/h$.

Assuming that $c = 10^{-2}$, $c_1 = 2 \cdot 10^{-5}$, $h = 10^{-1.8}$, $K_{\text{equilib}} = 10^{2.28}$, $a_H = 10^{14.12}$ we get $c - \varphi = 4.5 \cdot 10^{-5}$, from which the titration error is −0.45%. For $h = 10^{-1.7}$ $K_{\text{equilib}} = 10^{3.90}$ and $a_H = {}^{14.48}$ we get $c - \varphi = -6.8 \cdot 10^{-5}$, while the error amounts to +0.68%. For $h = 10^{-2.0}$, $K_{\text{equilib}} = 10^{4.89}$, $a_H = 10^{13.40}$ we get $c - \varphi = -1.88 \cdot 10^{-4}$, and the titration error is +1.88%.

SUMMARY

A study has been made of the interaction of trivalent thallium with certain complexonometric indicators: 1-(2-pyridylazo)-2-naphthol, 1-(2-pyridylazo)-resorcinol, and xylenol orange. The composition of the compounds formed by trivalent thallium ions with the reagents indicated has been determined, as well as the equilibrium constants of the complex formation reaction. The molar extinction coefficients of the compounds formed have been calculated. The pH conditions have been established at which the given indicators can be used during the complexonometric titration of trivalent thallium.

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SPECTROPHOTOMETRIC DETERMINATION OF ERBIUM AND HOLMIUM IN SOLUTION

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The absorption spectra of solutions of the salts of most of the rare earths possess a considerable number of narrow, intensive bands in the visible, ultraviolet, and infrared parts of the spectrum. Thanks to the characteristics of the structure of the electronic shells of these elements, their spectra depend to only a small extent on the structure and composition of complexes into which they enter, since the energy levels of the atoms between which transition of 4*f* electrons occur during absorption of light, are protected from the external influence of the filled electronic shell 5S5p. Accordingly, the spectrophotometric determination of the rare earths can be determined in simple solvents: water, alcohols, etc., without resorting to the use of complex organic reagents.

Only a relatively small number of papers have been published on spectrophotometric methods of determining the rare earths, since such methods are considerably less sensitive than the spectrographic method; on the other hand, the spectrophotometric method is more accurate than the spectrographic method. Among recent papers the most interesting are those of Polyakov and Rusanov [1], Wylie [2], and Moeller and Brantley [3]. In [1], which is devoted to the description of a technique for the determination of Pr, Nd, Sm, and Er, a study was made of the effect of other rare earths on the experimental results. In [2] is given a method for the determination of Pr, Nd, and Sm in solution, and a study was made of the effect of the presence of free acid, the ions of other rare earths, and neutral salts. In [3] the absorption spectra of 11 rare earths were measured, these rare earths being in solution in the form of various salts. In developing analytical methods, the effect of the slit width of the spectrophotometer and the presence of foreign anions was taken into account.

We have developed a method for the spectrophotometric determination of Er and Ho in pure aqueous and alcoholic solutions, and in solutions containing dysprosium salts.

The absorption spectra of the chlorides of Er, Ho, and Dy in water and in methanol were carefully measured on a SF-4 spectrophotometer in the region 220-1200 mμ.

By comparing the spectra obtained it was established that the most suitable bands for analytical purposes are 522.2 mμ in aqueous solutions (520.8 mμ in alcoholic solution) for Er, and 536.8 mμ (537.0 mμ in alcoholic solution) for Ho. There are no other intense bands near these, absorption in which could distort the experimental results; the background of the main absorption edge is almost completely absent, so that it is not possible to choose more intense bands in the ultraviolet part of the spectrum. The absorption is high enough – density $D = 0.380$ and $D = 0.267$, respectively, for 1% solutions of the chlorides of Er and Ho at a layer thickness of 10 mm. There are no characteristic Dy absorption bands near these bands, so that it is possible to determine Er and Ho spectrophotometrically in Dy solutions.

The absorption bands of Er and Ho chosen for analytical purposes have, however, a complex structure (see Figs. 1 and 2). It was necessary therefore to study the effect of changes in the concentration of the solutions on the ratio of the components of the complex bands in order to eliminate errors which might arise as a result.

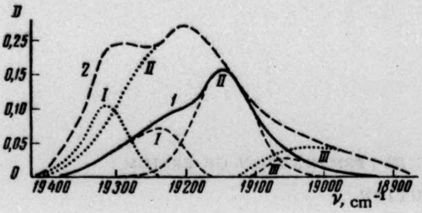

Fig. 1. Absorption band of erbium chloride at 522.2 mμ: 1) aqueous solution; 2) alcoholic solution.

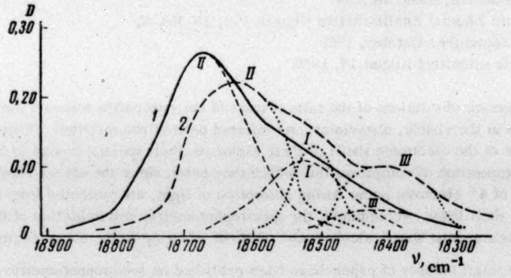

Fig. 2. Absorption band of holmium chloride 536.8 mμ: 1) aqueous solution; 2) alcoholic solution.

Resolution of the complex bands into components was carried out on the basis that their shape should correspond to a Gaussian probability curve. The correctness of this hypothesis is confirmed by the work of Jørgenson [4], in which a detailed examination was made of the shape of the absorption bands in the spectra of salts of elements with incomplete shells, on the basis of a vast amount of experimental data, and in which it was shown that they should have the shape of a Gaussian probability curve. The contour of the complex absorption band of Er^{3+} in aqueous solutions (Fig. 1) has one peak, on the short-wave wing of the contour there is clearly visible a protrusion, while on the long-wave wing there is a very slow drop starting at a density equal to half the maximum density. The contour of the absorption band of Er^{3+} in alcoholic solution is similar to that described, but instead of the protrusion there is a clearly manifested second peak. A study of both contours by the method described previously [5] showed that their long-wave wings are strictly Gaussian for densities $\geq 1/2\ D_{max}$. A preliminary analysis of the sum of the artificially constructed Gaussian curves showed that when the half widths do not differ strongly from each other, then in the case where there is a clearly manifested protrusion or a second peak on the total curve, it is possible to regard the wing of the more intense component as undistorted. Assuming that this rule holds for the experimental curves studied, we completed the contour of the most intense component on the basis of the measured segment of the total curve having a Gaussian form. The remaining two components were obtained by subtracting the constructed Gaussian curve from the measured contour of the band. When this was done it was found that the inner wings of the components obtained by subtraction also have the shape of a Gaussian curve, while the outer wings differ slightly from such a curve, particularly towards the ends, which is possibly caused by the influence of the total absorption background. The following parameters were determined for all the components: the absorption at the maximum D_0 and the frequency of the maximum ν_0 (by the numerical differentiation method), the half width of the band Δ (directly from the contour) and the area S confined by the contour and the frequency axis (by calculation for the Gaussian band, and by measurement with a planimeter for the other two).

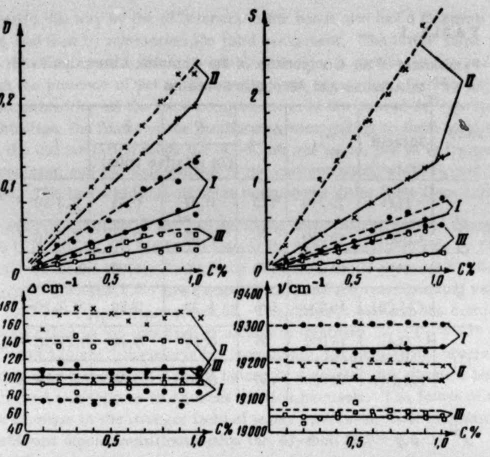

Fig. 3. The relation between the absorption parameters of a complex band and the concentration of the solution: 1) aqueous solution; 2) alcoholic solution.

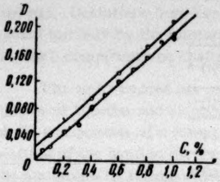

Fig. 4. Beer's law for solutions containing 5% dysprosium. The density values are slightly higher than the density of a pure solution of erbium because of the presence of insignificant amounts of erbium in the dysprosium.

In Fig. 2 their relationship to the concentration of Er^{3+} ions in water and in methanol is shown. The spectra were studied within the concentration range 0.05 to 1.0% Er. The position of all three components in the spectrum, and their half widths are constant, and are independent of the concentration; Beer's law is strictly obeyed and the areas are proportional to the concentration. The half widths in the spectrum of an aqueous solution are similar to each other, while in the spectrum of an alcoholic solution the half width of the first component is twice the half width of the second and third components. The large scatter in the points corresponding to the third component is explained by its low intensity and the difficulty of determining its parameters, which is connected with this. The forces of the oscillators for all the components were calculated by Kravets's method [6].

A comparison of the parameters of the corresponding bands in the spectra of the aqueous and alcoholic solutions shows that all the bands in the spectra of the alcoholic solutions are shifted towards the short-wave side as compared with the spectra of aqueous solutions, the distance between the components in the first case being greater than that in the second case ($\nu_I - \nu_{II}$ = 90 cm^{-1} and $\nu_{II} - \nu_{III}$ = 100 cm^{-1}, respectively). On switching from aqueous to alcoholic solutions, components II and III behave similarly; the half widths of the bands Δ, the absorption coefficients at the maximum D_0, and the forces of the oscillators increase: $\Delta_{MeOH}/\Delta_{H_2O}$ = 1.75 and 1.49; D_{MeOH}/D_{H_2O} = 1.32 and 2.73; f_{MeOH}/f_{H_2O} = = 2.36 and 2.73, for components II and III, respectively. The change in the parameters of the first component is somewhat different: on switching from aqueous to alcoholic solutions the half width of the band decreases: $\Delta_{MeOH}/\Delta_{H_2O}$ = 0.68, while the absorption coefficient and the oscillator force increase: $\Delta_{MeOH}/\Delta_{H_2O}$ = 1.75 and D_{MeOH}/D_{H_2O} = 1.30. It is known that an increase in the half width of a band is usually related to an increase in the interaction of the absorbing ion with the medium, while the growth of the absorption coefficient and the oscillator force are connected with an increase in the probability of a transition between levels.

TABLE 1

Parameters of the Components of the Complex Absorption Band of Er^{3+} in Aqueous and Alcoholic Solutions

Band No.	Solvent	ν_0, cm^{-1}	Δ, cm^{-1}	D	S	f
				(in relative units)		
I	H_2O	19 240	110	0,37	0,41	$2{,}3\cdot10^{-6}$
	CH_3OH	19 300	75	0,65	0,55	$3{,}0\cdot10^{-6}$
II	H_2O	19 150	100	1,00	1,00	$0{,}55\cdot10^{-5}$
	CH_3OH	19 200	175	1,23	2,29	$1{,}3\cdot10^{-5}$
III	H_2O	19 050	95	0,19	0,14	$0{,}77\cdot10^{-6}$
	CH_3OH	19 060	140	0,30	0,39	$2{,}1\cdot10^{-6}$

TABLE 2

Parameters of the Components of the Complex Absorption Band of Ho^{3+} in Aqueous and Alcoholic Solutions

Band No.	Solvent	ν_0, cm^{-1}	Δ, cm^{-1}	D	S	f
				(in relative units)		
I	H_2O	18 670	170	1,00	1,00	$1{,}33\cdot10^{-5}$
	CH_3OH	18 620	160	0,87	0,79	$0{,}96\cdot10^{-5}$
II	H_2O	18 540	175	0,41	0,45	$5{,}45\cdot10^{-6}$
	CH_3OH	18 545	90	0,48	0,25	$3{,}02\cdot10^{-6}$
III	H_2O	18 430	120	0,24	0,17	$2{,}06\cdot10^{-6}$
	CH_3OH	18 405	125	0,39	0,31	$3{,}75\cdot10^{-6}$

Accordingly, the experimental results considered enable one to assume that components II and III belong, apparently, to the same system of levels, while component I belongs to another, since the change in the half width for these components, on changing the solvent, occurs in opposite directions. Probably the system of levels corresponding to band I in the case of the Er^{3+} ion, when it is in alcoholic solution, is lower with respect to the system of levels corresponding to bands II and III than in aqueous solution. Both systems of levels split up more strongly in a field of CH_3OH molecules than in a field of H_2O molecules, which leads to an increase in the force of the oscillators for all three bands in alcoholic solutions. The value of the oscillator force indicates that the bands owe their origin either to dipole transitions inside the $4f$ shell of Er^{3+}, or to intercombination transitions.

Resolution of the complex band of Ho at 537.0 mμ in the spectrum of aqueous and alcoholic solutions was carried out in a similar fashion. The short-wave wing of the complex band has a Gaussian shape, while on the long-wave wing in the spectra of aqueous solutions, there is a clearly defined step, beyond which there follows a very slow drop towards longer wavelengths; two peaks are visible in the spectra of alcoholic solutions (Fig. 3). Taking into account, as before, that the short-wave wing of the band is the undistorted wing of the first component, we completed its Gaussian contour, and then subtracted it from the total contour of the curve. The short-wave wing constructed in this way by the differences in the bands also had a Gaussian shape, from this component II was determined, and then by subtraction, the third component. The latter third component was not strictly symmetrical. Its slow drop towards the long-wavelength side is possibly connected with superposition of the background, or with the presence of yet another component, separation of which was not achieved. The same parameters were determined for all the band components as in the case of Er^{3+} spectra: D_0, ν_0, Δ, and S as functions of the concentration; the forces of the oscillators corresponding to them were calculated. The solutions were studied within the concentration range 0.1-4.0%. It was found, just as in the case of the Er^{3+} spectrum that Δ and ν_0 are constant, and are independent of the concentration, while D_0 and S are directly proportional to the concentration. The half widths of all three components differ little from each other.

On switching from aqueous solutions of Ho^{3+} to alcoholic solutions appreciable changes in the spectrum are observed: components I, II, and III are displaced toward the long-wavelength side by 50, 25, and 25 cm^{-1}, respectively, while the half width and the oscillator force of bands I and II decrease by $\Delta_{H_2O}/\Delta_{MeOH} = 1.06$ and 1.95 and $f_{H_2O}/f_{MeOH} = 1.39$ and 1.80 times, respectively, and the corresponding values for band III increase $\Delta_{H_2O}/\Delta_{MeOH} = 0.97$ and $f_{H_2O}/f_{MeOH} = 0.55$. The distance between the components in the spectrum of aqueous solutions is greater than in the spectrum of alcoholic solutions: $\nu_I - \nu_{II} = 135$ cm^{-1} and 105 cm^{-1} and $\nu_{II} - \nu_{III} = 135$ cm^{-1} and 110 cm^{-1}, respectively. Presumably, the regularities observed in the spectra can be explained by considering that components I and II belong to a doublet, the distance between the upper levels of which, on switching from an alocholic to an aqueous solution, increases. The forces of the oscillators corresponding to these levels increase in the stronger field of water molecules; their magnitude is of the same order as oscillator forces for forbidden dipole transitions within the $4f$-shell $(1.0 - 0.5 \cdot 10^{-5})$.

Thus a detailed and careful analysis of all the parameters of the absorption bands enables one to expose those characteristics, on the basis of which it is possible, with known accuracy, to judge the differences in the origin of bands, which would be impossible if we had restricted ourselves to the usual study of the absorption at the maximum. A study of the structure of complex bands, and of the relationships that exist between the parameters of the components and the concentration, is also important for the purposes of spectrophotometric analysis. Deviations from Beer's law, which are often observed at high concentrations of the solutions, may be caused not only by the formation of new complexes and compounds, but also by differences in behavior of individual components on changing the concentration.

The study carried out on the absorption bands, which have been chosen for analytical purposes in the spectra of aqueous and alcoholic solutions of Er^{3+} and Ho^{3+}, has shown that differences in the characteristics of the components of a complex band have no effect on the results of spectrophotometric determinations. The position of the band in the spectrum does not depend on the concentration, while the absorption coefficient at the maximum D_0 is proportional to the concentration, and Beer's law is strictly obeyed within the limits investigated to 0.05 to 1.0% both in aqueous and alcoholic solutions of Ho and Er chlorides (Fig. 3).

A study was made of the effect on the experimental results of large amounts of Dy in the solution, taking as an example 5% solutions of Dy containing various amounts of erbium. It was found that Beer's law is strictly observed for these solutions also (Fig. 4).

The reproducibility of the suggested method, as determined from 10 replicate measurements, was found to be 3% for the concentration range 0.2-1.0%, and 5% for the concentration range 0.05-0.2%. The method can be recommended for the determination of Er and Ho in aqueous and alcoholic solutions containing Dy and other rare earths which do not have absorption bands in the part of the spectrum chosen for analysis.

In conclusion the authors wish to thank É. E. Vainshtein for his help in preparing this article.

SUMMARY

A quantitative method has been developed for the spectrophotometric determination of Er and Ho in aqueous and alcoholic solutions, in the presence of Dy and other rare earths which do not have absorption bands in the spectral region in which lie the absorption bands Er λ 522.2 mμ and Ho λ 536.8 mμ chosen for analysis. Determinations can be carried out within the concentration limits 0.05-1.0%; the accuracy of the method is 3-5%.

An analysis of the fine structure of the complex absorption bands chosen for analysis has been carried out. It has been shown that the parameters of the individual components of a complex band change differently on replacing the aqueous surroundings of the absorbing ions by an alcoholic one.

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PHOTOMETRIC DETERMINATION OF TITANIUM IN THE FORM OF A PYRIDINE-SALICYLATE COMPLEX

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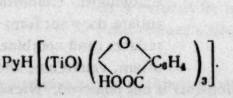
Original article submitted July 10, 1959

The peroxide method is usually used for the determination of small amounts of titanium in steel and other alloys. Determination of titanium in the form of a peroxide compound in the presence of a large amount of iron, chromium, vanadium, and other elements requires preliminary separation of titanium in the form of its cupferronate.

A photometric method* for the determination of titanium has been published, which is based on extraction of up to 99.8% of it at pH 3 by chloroform, in the form of the compound formed between titanium sulfosalicylate and tributylammonium. Tributylammonium is, however, not readily available. The chemical characteristics of the colored ternary compound of titanium are not given in this paper.

During a study of the salicylate complexes of titanium we established that at pH 3.5-5 a complex which is anionic in character is formed. This complex forms with certain organic bases (pyridine, quinoline, pyramidone, etc.) compounds which are sparingly soluble in water, but possess considerable solubility in chloroform. The compounds are intensely colored. During visual determination of the sensitivity, the yellow color was still observable at a titanium concentration of 10 μg in 25 ml of chloroform extract. We used this technique for developing a method for the photometric determination of titanium in steel.

A more detailed study has shown** that the compound formed is the pyridine salt of titanyl salicylic acid. On the basis of the analytical results and of a number of its properties, the following formula can be suggested for this compound



$$\mathrm{PyH}\left[(\mathrm{TiO})\left(\begin{matrix}\mathrm{O}\\ \mathrm{HOOC}\end{matrix}\!>\!\mathrm{C_6H_4}\right)_3\right].$$

The properties of this compound are similar to the properties of other ternary compounds formed in a system consisting of ion, metal anion, organic base.

In Fig. 1 is shown the absorption curve of a chloroform extract of the ternary complex of titanium, measured on a SF-4 spectrophotometer. To a solution containing $1 \cdot 10^{-4}$ g titanium was added 0.1 g each of sodium salicylate and the organic base. The pH of the solution prepared was adjusted to 3 and the solution extracted, the extracts were combined and then diluted with chloroform to 25 ml, after which the optical density was measured. The reference solution was chloroform which had been used for extracting a corresponding control solution free from titanium. The optical characteristics of the complex change little as a function of the organic base. When the titanium is extracted once, 89-96% of it is extracted, the percentage extraction increases slightly, in the order pyridine < quinoline < pyramidone.

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* Ziegler, H., Glemser, O., Bacckman A. U., Z. analyt. Chem. 160, 324 (1958).

** In the press.

In order to establish the optimum pH for the extraction, a solution of titanium salicylate (25 ml) containing $1 \cdot 10^{-4}$ g of titanium and 0.1 g of sodium salicylate was prepared. To this solution was added 0.1 g of the base (pyridine, quinoline, or pyramidone), the pH was adjusted to a definite value (using indicator paper) and the solution extracted 3-4 times with 5 ml lots of chloroform. The chloroform extracts were combined and the volume made up to 25 ml with chloroform, and the solution photometrically measured at 400 mμ in a cuvette with a layer thickness of 1 cm. The pH of the aqueous phase was checked with a quinhydrone electrode.

The results obtained are shown in Fig. 2. The optical density of the extracts of the pyridine- and pyramidone-salicylate complexes of titanium is plotted on the ordinate, while the pH of the aqueous phase is plotted on the abscissa. We established separately that extracts of the pyridine-salicylate complex of titanium conform to Beer's law. The optimum conditions for the extraction of the pyridine-salicylate complex is a pH of 3-3.5, while for the quinoline- and pyramidone-salicylate complexes the pH range is wider: 2.5-4.

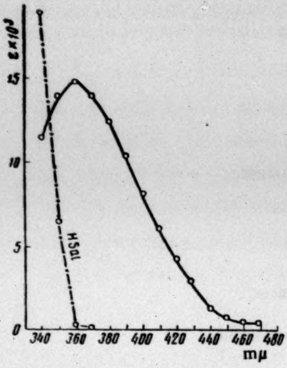

Fig. 1. Absorption curve of chloroform extracts of the pyridine-titanium salicylate complex. Titanium concentration $1 \cdot 10^{-4}$ M; layer thickness 1 cm.

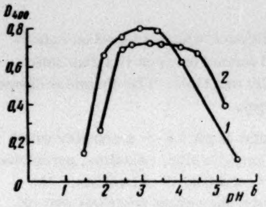

Fig. 2. Percentage extraction of the titanium-salicylate complexes with pyridine and pyramidone as a function of the pH of the aqueous phase. 1) Pyridine complex; 2) pyramidone complex; titanium concentration $1 \cdot 10^{-4}$ M.

Photometric determination of titanium. It was established in preliminary experiments that the salicylates of quinquevalent vanadium, divalent copper, and trivalent iron form with pyridine, quinoline, and pyramidone similarly colored ternary compounds which are readily extractable by chloroform. Sexivalent chromium reacts under the same conditions to form a yellow-colored compound but only with pyramidone, this compound is also extracted by chloroform. Chromium which has been reduced by thiosulfate does not form a colored compound. Thiosulfate reduces (and combines into a complex) iron, copper, chromium, vanadium, and other elements, so that formation of the colored ternary complexes of these elements is not observed. Nickel in the presence of sodium salicylate and pyridine at a pH of 4 and 5 is partially extracted by chloroform in the form of a blue compound. At pH 3.5, nickel is not extracted by chloroform.

On the basis of the results obtained we have developed the following method for the determination of titanium in steels. 0.1-0.2 g of steel (containing 1-0.1 mg Ti) is dissolved, as usual, in sulfuric acid (1 : 9) to which nitric acid has been added. The flask is boiled to remove nitrogen oxides, it is then cooled and the contents transferred to a 50-100 ml standard flask. Ten ml of this solution is transferred to a 50 ml conical flask in which it is neutralized with NH_4OH (1 : 1) solution to a pH of 1-2; 1-2 drops of 1% ammonium thiocyanate is added; this is followed by dropwise addition of a 10% solution of thiosulfate until the color of ferric thiocyanate has disappeared. 1-2 ml of a 10% solution of sodium salicylate is added; this is followed by 0.1 g pyridine (quinoline) or 5 ml of a 2% solution of pyramidone. The pH of the solution is adjusted to 3-3.5 by

Determination of Titanium in Steel

Standard sample	Content, %					Titanium found in %, on using:		Error in % (relative) on using:	
	Cr	Ni	Cu	V	Ti	pyridine	pyramidone	pyridine	pyramidone
83-e	0,11	0,09	0,22		0,12*	0,12	0,12	0	0
123^{a}	24,57	0,22	0,11		0,26	0,26	0,27	0	3,8
123^{a}	24,57	0,22	0,11	5*	0,26	0,26	0,27	0	3,8
52-a	17,49	9,60	0,21		0,41	0,41	0,42	0	2,4
52-a	17,49	9,60	0,21	10*	0,41	0,40	—	2,4	—
167	21,09	74,42	0,06		2,44	2,40	2,42	1,4	0,8
167	21,09	74,42	0,06	50*	2,44	2,48	—	1,6	—
87	12,55	0,55	—	2,26	0,12*	—	0,12	—	0

* Added.

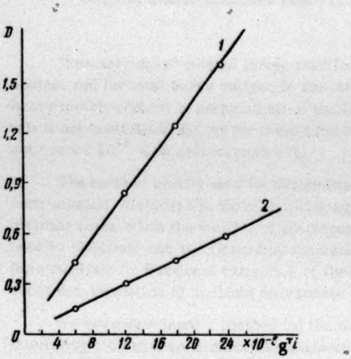

Fig. 3. Calibration curve for the determination of titanium in steel, in the form of its pyridine-salicylate complex. 1) at 400 mμ; at 430 mμ; layer thickness 1 cm.

means of ammonia (using indicator paper) and 10 ml of an acetate buffer with a pH of 3,5-3 added. The solution is transferred to a separating funnel, and is extracted 3-4 times with 4-5 ml lots of chloroform. The chloroform extracts are collected in a 25 ml flask, the volume is made up to the mark with chloroform and the optical density measured. The maximum light absorption of the compound, as is evident from Fig. 1, is found at 365 mμ; however, in this spectral region the absorption band of salicylic acid starts to appear. Accordingly, in order to avoid possible errors, and also to give a technique which is suitable for work with visual instruments, we carried out the photometric determinations at 400 or 430 mμ. At the same time, as can be seen from Fig. 1, the sensitivity increases (see also Fig. 3) at the lower wavelengths.

In Fig. 3 are shown the calibration curves for the determination of titanium in the form of its pyridine-salicylate complex. The solutions were prepared in the same way as indicated above for studying the absorption curves. The optical density was measured at 400 and 430 mμ. As is evident from the diagram, the test solutions conform to Beer's law.

The Table contains the results of determinations of titanium in several samples of steel. Determination of titanium in steel was carried out with the titanium in the form of both its pyridine-salicylate complex and its pyramidone-salicylate complex. The results given for the determination of titanium are the mean values of 6-8 determinations.

SUMMARY

A new method has been developed for the determination of titanium in steels. It is based on the extraction of the pyridine-(or quinoline, or pyramidone) salicylate complex of titanium at a pH of 3 with chloroform. The optical density of the yellow-colored extracts is measured at 400 or 430 mμ. Interference from iron, chromium, vanadium, and other interfering elements can be eliminated by treatment with the thiosulfate prior to extraction. The sensitivity of the method is 10 μg of titanium in 25 ml of extract.

EXTRACTION-PHOTOMETRIC DETERMINATION OF TRACES OF LEAD IN HIGH-PURITY REAGENTS

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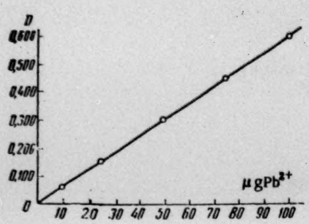
"Special purity" sodium iodide used for the preparation of crystallophosphors is controlled for its iron content and for total heavy metals, in the latter case thioacetamide in an alkaline medium is used [1]. The heavy-metals content in preparations of thallium iodide used for the activation of alkaline halide monocrystals is not controlled [2]. At the same time the content of lead which extinguishes the luminescence should not exceed 10^{-5} % in monocrystals [3].

The method usually used for determination of traces of lead and which involves extraction by a dithizone solution includes the use of masking agents, in particular potassium cyanide, which is toxic [4]. In individual cases, when the number of accompanying metal impurities is not large, selective determination of lead by dithizone can be effected by regulating the pH [5]. The most difficult problem is separation of lead from thallium by fractional extraction of their dithizonates in the presence of potassium cyanide, with subsequent decomposition of thallium dithizonate by potassium cyanide [4].

We have developed a method for the determination of traces of lead in thallium compounds in which interfering elements are removed by extraction. Thallium and iron are removed by extraction with oxygen-containing solvents in a hydrochloric acid medium; traces of lead, nickel, cobalt, manganese, and zinc are extracted in the form of their pyridine-thiocyanate complexes [6-9]. After removal of the macrocomponents and the microimpurities from the aqueous solution, lead diethyldithiocarbamate is extracted with chloroform. The lead content is determined by photometric measurement of the colored chloroform extract of copper diethyldithiocarbamate formed as the result of the equivalent substitution of lead ions by copper ions. The quantitative character of the exchange has been shown by a number of authors [10-13]. The behavior of sodium diethyldithiocarbamate at various pH values [14] indicates that it should be possible to use the method even at pH about 8.

A five g aliquot of thallium iodide is heated in a heat-stable beaker with 5 ml of water, 1 ml of concentrated sulfuric acid and 2 ml of concentrated nitric acid until fumes of sulfuric acid are evolved. The almost dry residue obtained is dissolved in 150 ml of hot water (when thallous sulfate is analyzed, an aliquot can be dissolved directly in water). To the solution obtained is added 10 ml of concentrated hydrochloric acid and 10 ml of hydrogen peroxide; the mixture is then slowly heated until the thallium chloride formed has dissolved completely. The solution is cooled and a further 10 ml of hydrogen peroxide added; it is then allowed to stand for 15 min in order to oxidize the thallium. Excess peroxide is removed by heating the solution and at the same time evaporating it to a volume of 2-3 ml. The solution remaining is transferred quantitatively to a 100 ml separating funnel, using 20 ml of 6 N hydrochloric acid for this purpose. The solution is extracted three times with 20 ml lots of isoamyl acetate; the organic layer is discarded. To the aqueous solution is added one drop of phenol red and the solution neutralized with ammonia until it is straw-yellow in color. Five ml of a 10% solution of ammonium thiocyanate is added next, followed by 1 ml of pyridine and 10 ml of chloroform;



Calibration curve for the determination of lead.

the solution is then extracted. The chloroform layer is discarded, while the aqueous layer is washed twice with 5 ml lots of chloroform. To the aqueous layer is added 30 ml of a mixture consisting of an ammonia-citrate buffer (pH about 8) and a 5% aqueous solution of sodium diethyldithiocarbamate in the proportion 2: 1, 10 ml of chloroform is added and the lead carbamate extracted by vigorous shaking for about 3 min. The chloroform layer is washed three times with water to free it from excess sodium diethyldithiocarbamate. For quantitative removal of traces of the chloroform extract from the aqueous wash liquors the latter are washed three times with 2-3 ml of chloroform, the chloroform washes being added to the main chloroform extract. Finally, to the extract is added 10 ml of a 0.01% solution of a copper salt in the ammoniacal-citrate buffer solution and the whole vigorously shaken for about 4 min. The yellow-colored chloroform layer is poured into a 25 ml standard flask, to this is added a few ml of chloroform used for washing the aqueous layer, after which the volume is made up to the mark with chloroform. The solution is filtered into a cuvette with a layer thickness of 5 cm and the optical density measured on a FÉK-M photocolorimeter fitted with a blue filter; the density is measured against chloroform as a reference. The optical density found during a blank run is subtracted from the optical density found for the test solution; in the blank run the solution is taken through all the operations described above using all the reagents mentioned; the lead content is then found from a calibration curve.

The calibration curve is constructed by introducing different amounts of Pb^{2+} (from 2.5 to 100 μg) into the separating funnel, 30 ml of the mixture of the ammoniacal-citrate buffer* and sodium diethyldithiocarbamate, and 10 ml of chloroform are added and the procedure outlined above then followed.

The reagents used were subjected to special purification. The water was distilled, while pyridine, nitric, and hydrochloric acids were purified by distillation in pyrex apparatus; the ammonia solution (s.gr. 0.95) was prepared by saturating twice-distilled water with gaseous ammonia; cupric sulfate, ammonium thiocyanate (chemically pure grade) and sodium diethyldithiocarbamate [14] were purified by recrystallization; the mixture of the solutions of ammoniacal-citrate buffer and sodium diethyldithiocarbamate was purified by shaking with chloroform until a completely colorless chloroform layer was obtained; the hydrogen peroxide and chloroform used were "medical" grade; the sulfuric acid passed the Saval test; the sodium iodide was a highly pure preparation with a lead content of $3 \cdot 10^{-5}$ %.

The results of all the measurements were treated statistically at a confidence level of 0.95 [16]. The calibration curve (diagram) which was constructed by the method of least squares [17] for the concentration range 3 to 100 μg, the number of measurements being equal to 16, showed good conformity to Beer's law. The error in measuring D is ± 3.4% (relative).

A study was made of the possibility of determining lead in the presence in the original solution of copper, nickel, cobalt, manganese, iron, and zinc ions in amounts one thousand times greater than the lead content. It was shown that these ions are completely removed during the extraction of their pyridine-thiocyanate complexes, and that they do not interfere with lead determination (Table 1).

In order to check the method, a known amount of a lead salt was added to a solution prepared from thrice-recrystallized thallous sulfate** and containing 10 mg thallium, and the procedure outlined above followed. The lead content in μg was calculated by means of the empirical formula C = 164.5 D. Results of the statistical treatment of the data obtained [16] are given in Table 2.

The method could also be used for other thallium compounds (Tl_2O, Tl_2O_3, Tl_2CO_3, etc.) after treating an aliquot of the corresponding preparation with concentrated sulfuric acid.

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* The buffer is prepared by neutralizing a 20% solution of citric acid with ammonia using phenol red as indicator; the neutralization is carried out to the point at which raspberry color appears.

** The lead content of the Tl_2SO_4 preparation did not exceed $7.2 \cdot 10^{-5}$ %.

TABLE 1

Separation of Foreign Metals during the Pyridine-Thiocyanate Extraction

Introduced		Optical density, D	Introduced		Optical density, D
Pb^{2+}, μg	foreign metal ion, 1000 μg each		Pb^{2+}, μg	foreign metal ion, 1000 μg each	
—	—	0,056	—	Fe^{3+}	0,052
—	Cu^{2+}	0,048	—	Zn^{2+}	0,058
—	Ni^{2+}	0,052	—	Cu^{2+} Ni^{2+} Co^{2+} *	0,053
—	Co^{2+}	0,046	10	—	0,108
—	Mn^{2+}	0,058	10	Cu^{2+} Ni^{2+} Co^{2+} Mn^{2+} Fe^{3+} *	0,104

* Introduced simultaneously

TABLE 2

Determination of Lead in Thallous Sulfate (10 mg of Tl_2SO_4 was added to the working and control solutions)

Pb^{2+} introduced, μg	Pb^{2+} found, μg	Results of statistical treatment	Pb^{2+} introduced, μg	Pb^{2+} found, μg	Results of statistical treatment
5,0	5,4	Dispersion	10,0	9,5	Error ± 5,6% (relative)
5,0	4,3	$S^2 \cdot 10^4 = 54,5$	25,0	25,0	
5,0	4,6	Precision	25,0	26,0	
10,0	9,0				
10,0	9,9	$\delta_{0,95} = \pm 0,056$	25,0	24,2	

TABLE 3

Determination of Lead in Sodium Iodide (10 g of NaI was added to the working and control solutions)

Pb^{2+} introduced, μg	Pb^{2+} found, μg	Results of statistical treatment	Pb^{2+} introduced μg	Pb^{2+} found, μg	Results of statistical treatment
3,0	3,3	Dispersion	5,0	4,9	Error ± 5.6% (relative)
3,0	3,0	$S^2 \cdot 10^4 = 16$	5,0	5,3	
3,0	3,0	Precision	25,0	25,8	
5,0	5,1	$\delta_{0,95} = \pm 0,033$	25,0	26,3	

The following technique was developed for the determination of lead in sodium iodide of special purity.

Ten g of sodium iodide was dissolved in 30 ml of water and the solution transferred to a 100 ml separating funnel, 3 ml of a 1% solution of sodium thiosulfate (for combining with the iodine) was added, followed by two drops of phenol red and the solution acidified with 6 N hydrochloric acid until its color is a straw-yellow. The pyridine-thiocyanate extraction was then carried out and all the subsequent operations described above carried out.

Results for the determination of lead in sodium iodide are given in Table 3.

SUMMARY

A method has been developed for the determination of down to $6 \cdot 10^{-5}$ g of lead in thallium compounds without using potassium cyanide.

It has been shown that lead can be determined after removal of one thousand times its amount of various cations.

The method is used for the determination of down to $3 \cdot 10^{-5}$% in sodium iodide of special purity.

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**Original Russian pagination. See C. B. translation.

COMPLEXONOMETRIC DETERMINATION OF BISMUTH AND LEAD IN BISMUTH-LEAD ALLOYS

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Bismuth-lead alloys, in particular eutectic alloys, are used in nuclear technics as a coolant [1-3]. The chemical methods used for determining lead and bismuth in each others presence are laborious and are not accurate enough. Thus, the well-known chromate method of determining lead at high bismuth contents, as a rule, gives high results for lead as a result of coprecipitation of bismuth. The error amounts to 1-3%.

The achievements of complexonometry in recent years lead one to suggest that of the chemical methods of analyzing bismuth-lead alloys, a complexonometric analysis would appear to be the most convenient with respect to the speed with which it can be carried out and with respect to the accuracy. Moreover, in contrast to other methods, successive direct determination of both components on one aliquot would appear to be possible. Complexonometric titration of various combinations of elements [4], including the pair Bi: Pb [5] is possible. Bismuth can be titrated directly with sodium ethylenediaminetetracetate (EDTA-Na) at pH 1-2, and lead at pH 4-6 [4, 6, 7]. In these cases it is expedient to use metal indicators which react with both bismuth and lead at the corresponding pH values. Such indicators include: pyrocatechol violet [8-11], pyrogallol red [12], bromopyrogallol red [13], methyl thymol blue [14, 15],* xylenol orange [5, 15, 16], hematoxylin [17, 18], 1(2-pyridylazo)-2-naphthol [7,19].**

Having tested all the indicators mentioned we settled on xylenol orange as the most sensitive one and the one giving the most contrasting color change: raspberry-red to yellow for bismuth and raspberry to lemon-yellow for lead.

As a result of work which we carried out we have developed a direct complexonometric method for the determination of the components of bismuth-lead alloys using xylenol orange as metal indicator; this method is superior to current methods in accuracy and rapidity.

The method has been checked on synthetic mixtures containing various ratios of bismuth and lead, analysis being carried out both by titrations of aliquots of solutions.***

As the results in Table 1 show, successive determination of bismuth and lead gives satisfactory results. As a rule, the error does not exceed the permissible error for titrimetric methods of analysis. Moreover, the method gives reliable results over a fairly wide range of ratios of Bi to Pb (1: 10 to 10: 1).

Experimental procedure. Titration of aliquots. An aliquot of the alloy weighing about 0.1 g is placed in a 250 ml conical flask, 5-7 ml of nitric acid (1: 3) is added and the flask covered with a watch glass, the flask is heated on a sand bath until the alloy has completely dissolved (5-10 min); the solution is then diluted to

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* The article by A. N. Korolev and M. K. Koichev [15] was published when we had finished our work.

** For a review on the use of complexonometric indicators, see [19].

*** Both titration of aliquots of solutions and titration of aliquots of sample gave almost equally accurate results.

TABLE 1

Determination of Bismuth and Lead in Synthetic Mixtures (25 ml aliquots from a 250 ml solution were taken for analysis)

Bismuth			Bi : Pb	Lead		
introduced, g	found, g	error, % (relative)		introduced, g	found, g	error, % (relative)
0,8037	0,8036	−0,012	1 : 1	0,7998	0,7998	0,00
0,8068	0,8067	−0,012		0,8047	0,8029	−0,22
0,8111	0,8010	−0,012		0,8008	0,8009	+0,013
0,8056	0,8047	−0,11		0,8019	0,8009	−0,13
0,8097	0,8099	+0,025		0,8127	0,8123	−0,037
0,8078	0,8078	0,00	10 : 1	0,0753	0,0752	−0,13
0,7990	0,7994	+0,05		0,0745	0,0746	+0,13
0,8138	0,8136	−0,025		0,0642	0,0642	0,00
0,0816	0,0815	−0,12	1 : 10	0,8101	0,8107	+0,07
0,0894	0,0898	+0,45		0,7999	0,7998	−0,012
0,0888	0,0888	0,00		0,7987	0,7988	+0,013

TABLE 2

Analysis of Various Samples of Alloys (titration of aliquots of solutions; in the first six experiments 50 ml aliquots from a 250 ml solution were taken, while in the remainder 20 ml aliquots were taken from a 250 ml solution)

Sample No.	Wt. of aliquot, g	Bismuth				Lead			
		vol. of 0.01 M EDTA-Na used for titrating Bi, ml	Bi found, %	mean	deviation from the mean	vol. of 0,01 M EDTA-Na solution used for titrating Pb, ml	Pb found, %	mean	deviation from the mean
22 (turnings)	0,8063	42,83	55,51	55,53	−0,02	34,60	44,46	44,31	+0,15
	0,8053	42,75	55,48		−0,05	34,35	44,20		−0,11
	0,8026	42,70	55,60		+0,07	34,30	44,28		−0,03
25 (turnings)	0,8081	43,00	55,60	55,59	+0,01	34,50	44,23	44,18	+0,05
	0,8053	42,80	55,54		−0,05	34,40	44,26		+0,08
	0,8151	43,40	55,64		+0,05	34,65	44,04		−0,14
5 (sprigs)	0,8637	19.60	59,29	59,03	+0,26	13,60	40,78	40,79	−0,01
	0,8250	18,60	58,90		−0,13	13,00	40,81		+0,02
	0,8381	18,90	58,92		−0,11	13,20	40,79		0,00
6 (sprigs)	0,8186	18,30	58,40	58,43	−0,03	13,10	41,45	41,50	−0,05
	0,8304	18,60	58,52		+0,09	13,30	41,48		−0,02
	0,8416	18,80	58,36		−0,07	13,51	41,58		+0,08

50-60 ml with distilled water and 50-100 mg of urea added for preventing the nitrogen oxides from affecting the indicator, the pH is adjusted to 0.5-1.5 with ammonia (1:1) using universal indicator paper, 2-3 drops of a 0.5% aqueous solution of xylenol orange * is added and the bismuth titrated with 0.01 M EDTA-Na** until the color changes from raspberry-red to yellow. The volume of EDTA-Na solution used for titrating the bismuth is noted and the buret refilled.

To the flask is next added 10-15 ml of a 25% solution of urotropine (the pH is thereby adjusted to 4.5-5.5) and the lead titrated until the color changes from raspberry to lemon-yellow.

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*The 0.5% solution of xylenol orange is prepared as follows: 0.5 g of xylenol orange is dissolved in distilled water in a standard flask, 0.5 ml of hydrochloric acid (1:1) is added and the volume made up with water to 100 ml. The precipitate which appears after 4-5 days is filtered off. The indicator solution prepared in this way keeps for a long time. A 0.5% aqueous-alcoholic (1:1) solution of xylenol orange can also be used.

**In our work we used a 0.01 M solution of EDTA-Na prepared by dissolving the exact amount of the preparation. It is best to standardize the EDTA-Na solution against a solution of pure metallic lead [20].

Fifteen samples of bismuth-lead alloys have been analyzed by this method. The results obtained for some of the samples are given in Table 2.

The complexonometric method of determining the components of bismuth-lead alloys has the advantages of speed and accuracy over the chromate and other methods in use at present. The analysis can be speeded up even further, if the lead content is not determined directly but is calculated by difference.

In a six-hour working day it is possible to carry out up to 30 analyses of alloy samples (using titration of aliquots of the samples) for both components, while on titrating aliquots of solutions, up to 20 analyses can be carried out.

The mean experimental error for ten bismuth determinations is a) 0.11% (absolute) on titrating aliquots of sample; b) 0.08% (absolute) on titrating aliquots of solutions.

The mean experimental error for determination of lead is: a) ± 0.07% on titrating aliquots of sample and b) ± 0.06% for titration of aliquots of solutions. The error of a single determination is 0.2-0.3% relative.

SUMMARY

A method is described for the successive complexonometric determination of the components of bismuth-lead alloys in a nitric acid solution, using xylenol orange as indicator. The accuracy of the method is very high; for an approximately equal weight ratio of Bi and Pb the error of a single determination of each component does not exceed 0.2-0.3% (relative). In a six-hour day it is possible to carry out 20-30 analyses for both components.

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COMPLEXONOMETRIC DETERMINATION OF QUADRIVALENT PLUTONIUM USING ARSENAZO AS INDICATOR

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Very few titrimetric methods are known for the determination of plutonium; they have all been developed for trivalent plutonium and are applicable to only relatively pure solutions. Thus, Koch's cerimetric method [1] is not suitable in the presence of uranium and iron, while Milner's complexonometric method [2] was developed only for the determination of Pu^{III} in the solutions obtained on dissolving the metal in hydrochloric acid.

Methods of determining plutonium in its most usual valence state of four would be of considerably greater interest. Fritz [3] has described the titration of thorium with EDTA-Na using arsenazo as an indicator at pH 1.7-3.0; this same reaction occurs with yttrium, lanthanum, and other rare earths at pH 6-10, but with calcium and magnesium in strongly alkaline media only. Taking into account the similarity between quadrivalent plutonium and thorium, as well as the properties of arsenazo [4] and the conditions under which it interacts with many cations [5], it was hoped that it would be possible to make successful use of EDTA-Na and arsenazo for the determination of Pu^{IV} in the presence of uranium, lanthanum, americium, chromium, etc.

From the work of Foreman and Smith [6] it is known that Pu^{IV} interacts with EDTA-Na in the proportion 1:1 to form a compound which is stable even in strongly acid solutions (1 N HNO_3) in which the complexes of UO_2^{2+}, La^{3+}, and many other cations dissociate completely.

Experimental. Reagents: 1) the stock Pu^{IV} solution (about 0.01 M) was obtained by dissolving the pure metal in hydrochloric acid; the solution was evaporated three times to dryness with sulfuric acid, and the residue dissolved in 0.5 N HNO_3. The solution was standardized gravimetrically.

2) The EDTA-Na solution with a concentration of about 0.005 M was prepared by dissolving 1.86 g of the purified preparation in one liter of water. It was standardized against 0.190 M calcium chloride solution [7].

3) The indicator solution was a solution of 0.4 g of arsenazo in 100 ml water.

Pu^{IV} ions form a blue-violet colored compound with arsenazo; addition of excess EDTA-Na causes the color to change to rose. The definition of the endpoint depends on the acidity of the solution. Accordingly, the first series of experiments was designed to establish the optimum acidity (Table 1).

The color change was most clearly defined and the minimum error was obtained at an acidity of 0.1-0.2 N, at a plutonium concentration of about 0.1-0.2 mg/ml, and for an amount of indicator equal to 10-20 drops for 40-100 ml of the solution being titrated.

At low acidities the errors increase, probably as a result of hydrolysis and polymerization of plutonium ions; at high acidities (> 0.3 N) the colors (blue) indicate a relative decrease in the stability of the complex of plutonium with EDTA-Na.

TABLE 1

Pu^{IV} taken mg	Initial acidity, N	Final volume, ml	No. of drops of the indicator	Amount of 0.0051 M EDTA-Na solution used, ml	Pu, found	Error	
						mg	%
2,63	0,04	100	10	1,70	2,07	—0,56	—21,2
5,26	0,05	160	20	3,92	4,75	—0,51	—9,6
2,63	0,05	80	12	2,02	2,47	—0,16	—6,1
5,26	0,08	100	10	4,26	5,20	—0,06	—1,1
2,63	0,08	50	10	2,13	2,60	—0,03	—1,1
2,63	0,10	40	5	2,14	2,61	—0,02	—0,8
2,63	0,10	40	6	2,16	2,63	0	0
5,26	0,10	80	12	4,28	5,22	—0,04	—0,8
2,63	0,10	40	8	2,16	2,63	0	0
2,63	0,20	20	12	2,18	2,64	+0,01	+0,4
2,63	0,20	20	8	2,14	2,61	—0,02	—0,8
5,26	0,20	40	10	4,31	5,25	—0,01	—0,2
5,26	0,20	40	10	4,30	5,24	—0,02	—0,4
2,63	0,30	15	6	2,19	2,67	+0,03	+1,1
5,26	0,30	25	10	4,40	5,37	+0,11	+2,1
2,63	0,40	10	14	2,43	2,96	+0,33	+12,5
5,26	0,6	15	6	4,80	5,85	+0,59	+11,2
10,52	0,15	110	20	8,59	10,48	—0,04	—0,4
13,15	0,18	100	28	10,76	13,12	—0,03	—0,3
1,35	0,15	10	6	1,10	1,35	0	0
21,04	0,12	180	40	17,14	20,91	—0,14	—0,66
26,19	0,18	80	23	21,32	26,02	—0,17	—0,65
25,56	0,15	100	25	11,48	25,24	—0,32	—1,2

TABLE 2

Pu^{IV} taken, mg	Introduced, mg		Initial acidity, N	Initial volume, ml	No. of drops of the indicator	Amount of 0.0051 M EDTA-Na solution used, ml	Pu found, mg	Error	
								mg	%
2,63	La^{3+}	8,5	0,12	40	12	2,14	2,61	—0,02	—0,8
5,26	La^{3+}	18	0,15	60	12	4,28	5,22	—0,04	—0,8
2,63	UO_2^{2+}	10	0,15	30	10	2,18	2,64	+0,01	+0,4
5,26	UO_2^{2+}	40	0,15	60	15	4,28	5,22	—0,04	—0,8
1,42	UO_2^{2+}	100	0,15	20	15	1,18	1,44	+0,02	+1,4
1,42	UO_2^{2+}	200	0,15	30	25	1,22	1,48	+0,06	+4,2
1,42	UO_2^{2+}	100	0,12	50	15	1,14	1,39	—0,03	—2,1
1,42	UO_2^{2+}	200	0,12	50	23	1,14	1,39	—0,03	—2,1
2,63	Fe^{3+}	10	0,15	30	15	4,9(?)	?	—	—
5,26	Fe^{3+}	5	0,15	60	15	4,9(?)	?	—	—
2,63	Cr^{3+}	4	0,15	30	10	2,16	2,63	0	0
2,63	Cr^{3+}	10	0,15	30	10	2,18	2,65	+0,02	+0,8
2,63	Pb^{2+}	8	0,12	35	10	2,14	2,61	—0,02	—0,8
2,63	Ni^{2+}	5	0,15	30	10	2,16	2,63	0	0

The effect of other cations on the determination of Pu^{IV} depends on the stability of their compounds with ethylenediaminetetracetic acid and with arsenazo at the given acidity. The low stability of the complexonates of Ca, Mg, Zn, Al, Cd, and Mn in acid media ensures that they will have little effect; on the other hand, Th, Zr, and U^{IV}, which under these conditions give bright colors with arsenazo, should interfere even at low concentrations of these elements. Table 2 contains results for the determination of plutonium in the presence of the elements which usually accompany it.

TABLE 3

(Acidity 0.15 N)

Pu^{IV} taken, mg	Fe^{3+} introduced, mg	Initial volume, ml	No. of drops of the indicator	Amount of 0.0051 M EDTA-Na solution used, ml	Pu found, mg	Error	
						mg	%
2,91	0,045	15	8	2,39	2,91	—0—	—0—
2,97	0,045	15	8	2,44	2,97	—0—	—0—
2,91	0,09	15	8	2,39	2,91	—0—	—0—
2,97	0,09	15	8	2,46	3,00	+0,03	+1,0
2,97	0,09	15	8	2,44	2,97	—0—	—0—
2,91	0,15	15	8	2,40	2,92	+0,01	+0,3
2,97	0,15	15	8	2,50	3,05	+0,08	+2,8
2,91	0,23	20	10	2,46	3,00	+0,09	+3,0
2,97	0,23	20	10	2,55	3,11	+0,14	+4,9
2,84	0,40	15	10	2,76?	?	—	—

Experiments showed that uranyl ions even when present in amounts which were 140 times that of plutonium, do not rule out the possibility of determining plutonium. Of the elements which usually accompany plutonium, only Fe^{3+} ions interfere.

Iron can be tolerated in amounts of up to 3-4% of the plutonium at concentrations up to 1 mg in 100 ml (Table 3).

The titration conditions are as follows: amount of plutonium 2-20 mg, volume of solution 40-100 ml, acidity 0.1-0.2 N, indicator – 0.4% solution of arsenazo – 10-20 drops, EDTA-Na concentration 0.005-0.01 M. The endpoint can be conveniently established by means of a "reference" solution, which is a solution of the indicator under the same conditions of concentration and acidity.

SUMMARY

A method for determining Pu^{IV} is described; it is based on titration with 0.01-0.005 M solution of sodium ethylenediaminetetracetate (EDTA-Na) in an acid medium (0.1-0.2 N HNO_3 or HCl), using arsenazo I as an indicator. La^{3+}, UO_2^{2+}, Cr^{3+}, Pb^{2+} and Ni^{2+} do not interfere. Fe^{3+} must not be greater than 3-4% of the Pu content.

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POLAROGRAPHIC DETERMINATION OF TUNGSTEN*

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Separate polarographic determination of tungsten and molybdenum is of considerable interest, since they interfere with each other in the same supporting electrolyte; moreover, tungsten frequently does not give a wave in media in which molybdenum gives a clearly defined wave [1].

Data on the polarography of tungsten is very scant because W^{IV} is not reduced in either neutral or alkali media, although it is known to be reduced in hydrochloric acid. Lingane and Small [2] have studied the various oxidation states of tungsten in hydrochloric acid polarographically. Kolthoff and Parry [3] have observed a tungsten kinetic wave in the presence of hydrogen peroxide; the wave is not controlled by diffusion. Souchay [4] has made a polarographic study of various tungstates and heteropoly acids of tungsten. Von Stackelberg et al [5] have determined tungsten in steel using 9 N hydrochloric acid as supporting electrolyte. Recently, Meites [6] observed a well-defined tungsten wave in phosphoric acid. Reichen [7] has also used tartaric acid for the determination of the tungsten content of rocks.

During a search for a common electrolyte which would give clearly defined waves for Mo^{VI} and W^{VI}, it was noticed that in the presence of oxalic acid, under certain conditions, two clearly defined waves which are characteristic of the elements indicated are formed. Moreover, it was established that the oxalate ion prevents precipitation of the hydrated oxide of tungsten. The results obtained were used for the successive polarographic determination of molybdenum and tungsten in one solution. In addition it was also found possible to carry out separate determination of iron and tungsten.

Experimental. The polarograms were recorded at 25 ± 0.1° on a Leeds and Northrup electrochemograph type E. The reference electrode (a saturated calomel electrode) was connected to the electrolyzer via a potassium chloride – agar-agar bridge. The value of $m^{2/3} \cdot t^{1/6}$ for the capillary used varied in various experiments, since the drop time was not the same, while the weight of a mercury drop at 25° in distilled water, without an applied potential, was 7.568 mg. The pH was measured by means of a Beckman pH-meter.

The stock sodium tungstate solution was prepared by dissolving an aliquot of the chemically pure preparation in distilled water, the tungsten content was checked gravimetrically by the benzidene method.

Sodium oxalate (0.2 M solution) was used as complexing agent and as a supporting electrolyte for obtaining the tungsten waves. The pH of the solutions was regulated by addition of dilute sulfuric acid. The gelatin concentration was kept constant at 0.005%.

Characteristics of the polarographic waves. Preliminary studies were carried out with 0.2 M sodium oxalate containing 0.005% gelatin as maximum suppressor, and appropriate amounts of tungstate solution. The pH of the solution was altered by addition of dilute sulfuric acid. Polarographic waves only appeared at pH 2.0 (Table 1), but the wave height was so small that it could not be used for analytical purposes. On decreasing

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* Translated from English by Z. I. Podgaiskaya.

TABLE 1

Effect of the pH of the Solution on the Polarography of Tungsten

pH	$E_{1/2}$ (saturated calomel electrode)
8,5	Not reduced
4,5	Ditto
3,0	Ditto
2,0	Very small wave
0,8	−0,625
0,5	−0,61
0,05	−0,57

TABLE 2

Effect of Oxalate Concentration on the Polarography of Tungsten

pH	Oxalate concentration, M	$E_{1/2}$ (saturated calomel electrode)
0,7	0,5	−0,62
0,8	0,25	−0,615
0,6	0,20	−0,62
0,6	0,125	−0,61
0,6	0,10	−0,62
0,5	0,05	−0,62

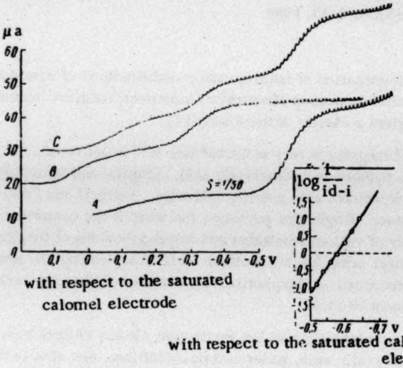

Fig. 1. Tungsten polarogram. Drop-formation time 3/5 sec; A) tungsten wave (5.95 mM) in an oxalate medium; B) molybdenum wave (2.33 mM) in an oxalate medium; C) polarogram of tungsten and molybdenum when the two are present together.

the pH further, better results were obtained and the waves were clearly defined. However, the half-wave potential was shifted toward more negative values on increasing the pH. This gives a basis for assuming that the oxalate complex of tungsten is more stable at the higher pH values, and that its stability is dependent on the acidity of the solution.

The half-wave potential remains constant and is independent of oxalate concentration within the limits 0.05-0.5 M (Table 2). However, well-defined waves appear in a medium of 0.2 M oxalate solution in the presence of 0.005% gelatin at a pH equal to or less than 1.0. When the polarograms were being recorded it was observed that the residual current increased when tungsten was present in solution, probably as a result of partial adsorption of tungsten anions on the mercury drop. This was confirmed by the fact that the residual current remained constant and was independent of the tungsten concentration.

The electrode reaction is reversible (Fig. 1). The wave was obtained in a solution containing 5.95 mM tungsten, 0.2 M sodium oxalate, and 0.005% gelatin as maximum suppressor. The relation between log $i/(i_d-i)$ and E is shown in Fig. 1. In accordance with the equation

$$E = E_{1/2} - \frac{0,059}{n} \lg \frac{i}{i_d - i}$$

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TABLE 3

Diffusion Current Constants

W concentration mM	i_d (observed)	i_d after correction for $i_d - i_{da}$	$i_d / Cm^{2/3} t^{1/6}$	I (corrected)
1,19	1,0	3,0	0,408	1,22
2,38	3,25	5,25	0,663	1,07
3,57	6,0	8,0	0,816	1,08
4,76	8,5	10,5	0,867	1,07
5,95	11,5	13,5	0,938	1,10
7,14	14,0	16,0	0,952	1,12
8,33	17,0	19,0	0,991	1,13
9,529	19,25	21,25	0,981	1,08
10,72	22,0	24,0	0,996	1,08
11,91	25,0	27,0	1,02	1,10
13,1	28,0	30,0	1,03	1,11
14,29	30,0	32,0	1,02	1,09
15,48	33,0	35,0	1,01	1,10
			Mean	1,1±0,03

TABLE 4

Determination of Tungsten and Molybdenum in Each Other's Presence

W^{VI} added, mM	W^{VI} found, mM	Mo^{VI} added, mM	Mo^{VI} found, mM
11,91	11,91	—	—
9,53	9,52	1,16	1,16
7,14	7,25	2,33	2,28
4,76	4,76	3,5	3,48
2,38	2,42	4,6	4,66

the experimental points fall on a straight line with a slope of 0.064 v. This corresponds to a one-electron transfer during reduction.

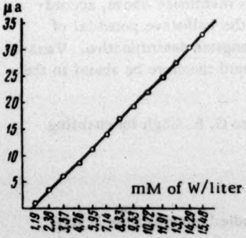

Fig. 2. Calibration curve for tungsten.

The diffusion current is directly proportional to tungsten concentration within the limits 1.19-16.67 mM. In more concentrated tungsten solutions, in the presence of oxalate ions, addition of gelatin caused the solution to become turbid, but did not affect the value of the diffusion current or the character of the wave. At higher acidities the limiting current is not very well expressed as a result of the liberation of hydrogen at the higher positive potentials.

The calculated constants of the diffusion current are given in Table 3. They decrease with decreasing tungsten concentration, but, as mentioned above, the values of the diffusion current are linearly related to the tungsten concentration. This unusual behavior may be explained by the calibration curve (Fig. 2), from which it follows that the diffusion current observed is only proportional to the tungsten concentration, while its actual value can be determined from the equation

$$i_d = IC + i_{da},$$

where i_d is the observed diffusion current, I is the constant of the diffusion current, C is the concentration of the reduced tungsten ion (M), and i_{da} is the adsorption current in μA. Thus, the value of the adsorption current which leads to an increase in the residual current, as determined by the curve, is 2.0 μA. This assumption is confirmed further by the fact that the mean increase in the residual current for all the tungsten concentrations studied is constant, i.e., equal to 2.0 μA. A further confirmation of this conclusion is given by experimental observations which show that on addition of any other ion which is reduced prior to the appearance of the adsorption current, the value of 2.0 μA is added to the actual height of the wave on the tungsten polarogram.

The diffusion coefficient of tungsten was calculated after applying the correction indicated above to the observed value of i_d and by substituting the values obtained in this way in the equation

$$I = 605n\sqrt{D}.$$

The diffusioncoefficient of the tungsten ion proved to be $3.3 \cdot 10^{-2}$ cm^2/sec. This value, obviously, is considerably higher than the value for the chromate ion; doubtless, tungsten is present in solution in the form of its oxalate complex. Since the constant of the diffusion current has a constant value, obviously, the extent of polymerization does not change on increasing the oxalate ion concentration.

Sexivalent molybdenum [8] is also reduced on a dropping-mercury electrode under the same experimental conditions as those for which clearly defined tungsten waves appear, and these waves do not interfere with each other. The results obtained were therefore used for the separate determination of Mo^{VI} and W^{VI}. It was observed that the first molybdenum wave is suppressed in the presence of tungsten ions, but the latter do not affect the over-all molybdenum wave. The results obtained are given in Table 4. A correction was applied to the diffusion current for the wave of the residual current obtained at the same potential value at which the wave height of molybdenum was calculated.

The presence of chlorides, sulfates, and bisulfates of the alkali metals does not affect the tungsten polarogram. Nitrate ions lead to an increase in wave height but do not distort its shape. Probably, the current increases as the result of a catalytic reduction of nitrate ions under the experimental conditions; nitrate ions should therefore be absent.

The possibility of determining tungsten in steel was studied. In this connection the effect of iron, nickel, chromium, manganese, and vanadium ions on the tungsten wave was examined.

Iron is reduced in 0.2 M oxalic acid to give a well-defined wave. Although the value of $E_{1/2}$ for iron is strongly dependent on pH, while the wave height is dependent on the photochemical action of light [9], the half-wave potential of iron is far removed from that of tungsten. Use can be made of this fact in recording polarograms for solutions containing tungsten and iron.

Chromium, manganese, and nickel ions are not reduced under the conditions mentioned above, accordingly, the iron and tungsten waves are readily distinguishable. Iron does not shift the half-wave potential of tungsten. Copper is precipitated as its oxalate, and thus does not interfere with tungsten determination. Vanadium gives a wave and completely distorts the tungsten polarogram, vanadium should therefore be absent in the solution of steel being polarographed.

We wish to thank S. S. Joshi for help in this work and for his advice, and also G. B. Singh for enabling this work to be carried out.

SUMMARY

Reduction of sexivalent tungsten on a dropping-mercury cathode has been studied using oxalate as supporting electrolyte. A method has been developed for the successive determination of molybdenum and tungsten in a common supporting electrolyte. It has been shown that it is possible to determine iron and tungsten separately.

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AN EXTRACTION-PHOTOMETRIC DETERMINATION OF TRACES OF IRON BY MEANS OF 1-NITROSO-2-NAPHTHOL

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Of primary importance for scintillation materials is freedom from traces of iron which is a luminescence extinguisher [1]. In a search for highly sensitive and selective reactions for iron we settled on extraction of the intensely green-colored complex of Fe^{2+} with 1-nitroso-2-naphthol, the absorption curve of which in isoamyl alcohol is shown in Fig. 1. This complex was described long ago by Il'inskii and Knorre [2]. Fischer [3] has indicated the possibility of an extraction-photometric determination of iron. Vanosi [4] has extracted the compound of divalent iron formed with ethyl acetate during detection of iron by a spot method.Kozo Sone [5] studied the compound of Fe^{2+} and 1-nitroso-2-naphthol among a number of other anomalously colored inner-complex compounds of iron. While working with a solvent in which the complex is rapidly oxidized in the air, the author, however, established from spectrophotometric methods that its composition corresponds to a ratio of addendum to iron of 3:1.

Reagents, solutions, and measurement technique. A stock solution of ferric sulfate (1000 μg/ml) was prepared by oxidizing Mohr's salt (recrystallized chemically pure grade) in a sulfuric acid medium with hydrogen peroxide (medical). The concentration of the stock solution, from which the working solutions were prepared subsequently, was checked titrimetrically [6]. The solutions of the salts of the other metals were prepared from the recrystallized or chemically pure preparations. All the solutions of the metal salts were acidified with sulfuric (chemically pure) or nitric (redistilled from chemically pure acid) acid.

The organic solutions used were either chemically pure or analytical-grade materials; some of them were subjected to additional purification.

Ascorbic acid (medical, 10% solution) was dissolved in water saturated with CO_2, and stored in a darkened flask connected with a buret for measuring out the solution, and with a carbon dioxide source.

Solutions of 1-nitroso-2-naphthol were prepared by dissolving aliquots of the reagent in 120 ml of 1 N potassium hydroxide (chemically pure), and were purified from metals by shaking with chloroform, after which the solution was filtered and diluted with water to 1 liter.

Tartaric (analytical grade) and citric (chemically pure) acids, sodium hydrogen phosphate (recrystallized chemically pure), and sodium iodide (special purity), were used. Ammonia solutions were prepared by saturating water with gaseous ammonia. The water which was used was distilled twice in pyrex apparatus.

The extractions were carried out in separating funnels whose stopcocks were free from grease. The optical density was measured on a FÉK-M photoelectricolorimeter, and the pH on a LP-5 pH-meter fitted with a glass electrode. The absorption curves were taken on a SF-4 spectrophotometer. The results of all the measurements were treated statistically [7] at a confidence level of 0.95.

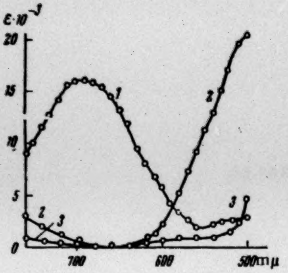

Fig. 1. Absorption curves of the compounds of divalent iron (1) cobalt (2), and nickel (3) with n-nitroso-2-naphthol in isoamyl alcohol. SF-4 spectrophotometer; concentrations of the solutions in isoamyl alcohol: 0.2, 2, and 2 μg of metal per ml,* respectively; cuvette with a layer thickness 10 mm.

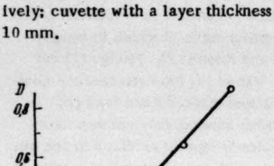

Fig. 2. Calibration curve for the determination of iron with 1-nitroso-2-naphthol.*

Experimental conditions. CCl_4, $CHCl_3$, benzene, toluene, ethyl acetate, isoamyl acetate, and dichloroethane proved unsuitable for the extraction of the complex of Fe^{2+} with 1-nitroso-2-naphthol on account of the flotation of the particles of the complex on the interface, and also because of the considerable weakening of the color of the extracts on standing. Isoamyl alcohol proved to be the best solvent.

In choosing a reducing agent we settled on ascorbic acid, although hydroxylamine hydrochloride can be recommended in certain cases. The latter permits determination in an acetate medium, but it is not completely suitable in the presence even of comparatively small amounts of tartrate or citrate ions. Ascorbic acid, as is evident from the results given below, permits determination to be carried out in the presence of large amounts of masking agents, which usually interfere with iron determination.

The optimum pH for reduction with ascorbic acid is 7.5 ± ± 0.5. This pH is readily established by neutralizing the aqueous solution of tartaric, citric, or phosphoric acids with ammonia using phenol red as indicator.

Construction of a calibration curve. Twenty ml of tartaric acid (0.05 M solution containing 15-20 drops of phenol red*) was introduced into a separating funnel, this was followed by a measured volume of the standard ferric sulfate solution, and 5 ml of ascorbic acid. After the solution has been neutralized with ammonia to the phenol-red end point, 5 ml of the 1-nitroso-2-naphthol solution (0.2 g/liter) was added to the funnel, and, after 40 min, extraction was carried out with two lots of 10 ml of isoamyl alcohol. The combined extract was diluted with solvent to 25 ml in a standard flask and the optical density measured in a cuvette with a layer thickness of 5 cm using a red filter, measurements were made relative to the extract obtained in a control experiment (this extract differed from the working solution only in that the ferric sulfate solution was replaced by an equal volume of water, acidified in the same way as the working solution with sulfuric acid). Twenty-nine experiments carried out in order to get five points on the calibration curve showed that Beer's law is closely obeyed within the range 0.5-20 μg Fe. The slope of the calibration curve (optical density D – amount of Fe in μg) calculated by the method of least squares [7, 8] proved to be 0.4292 ± ± 0.00007; the deviation of the value of a free member from zero can be related to random causes (the straight line passes through the origin). The calibration curve is shown in Fig. 2.

Effect of foreign ions. Experiments with metallic ions were carried out by the same procedure as that adopted for constructing the calibration curve (a known amount of the salt of the respective metal was introduced into the working solution, as well as the iron salt). In experiments with masking agents, a measured volume of tartaric, or citric acid, or sodium monohydrogen phosphate, acidified with sulfuric acid was added to the separating funnel, this was followed by 15 ml of ascorbic acid solution, after the solution had been neutralized with ammonia, 5 ml of the 1-nitroso-2-naphthol solution (1 g/liter) was added and the solution diluted with water to 150 ml. The control experiment differed from the test experiment only in that the ferric salt solution was replaced by the corresponding volume of water acidified with sulfuric acid. The experimental results obtained are given in Table 1.

Since the nitroso-naphtholates of most metals, as well as the reagent itself, in contrast to ferrous naphtholate, do not have absorption bands in the red part of the spectrum, iron can be determined, as is evident

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* A 0.1% solution in 20% ethanol.

TABLE 1

Determination of Iron in the Presence of Foreign Ions (5 μg Fe^{3+} taken)

Foreign ion X, mg	Ratio Fe : X*	No. of expt., n	Fe found, μg	Foreign ion X, mg	Ratio Fe : X*	No. of expt., n	Fe found, μg
Ag^{+}—0,05	1 : 10	3	5,13±0,48	Pb^{2+}—5	1 : 1000	3	4,89±0,49
Al^{3+}—5	1 : 1000	3	5,05±0,38	Tl^{+}—5	1 : 1000	3	5,15±0,48
Cd^{2+}—5	1 : 1000	3	4,96±0,59	UO_2^{2+}—0,5	1 : 100	3	5,14∓0,48
Co^{2+}—0,02	1 : 4	5	5,34±0,49	Zn^{2+}—5	1 : 1000	3	5,02±0,33
Cu^{2+}—0,4	1 : 80	5	4,89±0,22	Zr^{IV}—4	1 : 800	3	4,81±0,63
Ni^{2+}—0,025	1 : 5	5	5,31±0,47	Cit^{3-}—740	$1 : 1,5\cdot10^{5}$	5	4,93±0,25
Mn^{2+}—5	1 : 1000	3	5,19±0,59	PO_4^{3-}—3580	$1 : 7,2\cdot10^{5}$	5	4,96±0,27
MoO_4^{2-}—0,5	1 : 100	3	5,14±0,44	$Tart^{2-}$—4440	$1 : 8,9\cdot10^{5}$	5	5,04±0,22

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* In those cases where Fe : X > 1 : 1000, and also for Cit^{3-}, PO_4^3, and $Tart^{2-}$, the ratios adduced in the test conditions are limiting values.

TABLE 2

Determination of Iron in Sodium Iodide (10 g of NaI and Fe^{3+} were introduced into the test solution, and 10 g of NaI into the control)

Fe^{3+} introduced, μg	No. of determinations, n	Arithmethic mean for the values found μg ($\bar{x}$)	Dispersion $S^2\cdot10^4$	Accuracy, δ ± 0.95	Error, % (relative)
0,5	7	0,544	63,8	0,074	14,8
1	7	1,08	197,2	0,13	13,0
5	5	5,09	215,2	0,18	3,6
20	5	19,86	893,7	0,37	1,9

TABLE 3

Determination of Iron in Tartaric Acid (4.5 g of tartaric acid and Fe^{3+} were added to the test solution, while only 4.5 g of tartaric acid was added to the control)

Fe^{3+} added, μg	No. of determinations, n	Arithmetic mean for the values found, $\bar{X}$	Dispersion $S^2\cdot10^4$	Accuracy $\pm\delta_{0.95}$	Error, % (relative)
1	7	1.04	239.5	0.14	14.0
5	5	5.04	325.2	0.22	4.4
10	5	9.94	272.5	0.21	2.1
20	5	19.87	649.7	0.32	1.6

from Table 1, even the presence of moderate amounts of Co^{2+} and Ni^{2+}. The absorption curves of the respective naphtholates in isoamyl alcohol are shown in Fig. 1. Cu^{2+} ions, apparently, are reduced under the given conditions and do not form a colored complex with 1-nitroso-2-naphthol; however, in the presence of large amounts of Cu^{2+} the results for iron were low. Determination of iron cannot be carried out in the presence of large amounts of Ag^{+}, since this cation is reduced by the anion of ascorbic acid in an alkaline medium to the metal.

Determination of iron in "special purity" sodium iodide and in tartaric acid. Sodium iodide and other alkali metal halides used for producing scintillation monocrystals have to be highly pure. The methods suggested for determination of iron in this preparation [9, 10], however, are not sensitive enough ($1\cdot10^{-4} - 2.5\cdot10^{-5}$ %).

TABLE 4

Reproducibility of the Determination of Iron in Sodium Iodide and Tartaric Acid

Preparation	No. of determinations, n	Arithmetic means for the values found (in μg Fe per g preparation)	Dispersion, $S^2 \cdot 10^4$	Accuracy, $\pm \delta_{0.95}$	Error, % (relative)
Sodium iodide "special purity" m = 10 g	4	0.713	6.61	0.041	5.8
Tartaric acid, analytical grade Δm = 4 g*	5	1.73	19.47	0.055	3.2

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* $m_1 = 4.5$ g, $m_1 = 0.5$ g, $\Delta v_{NH_3} = 14.9$ ml, $q = 8.4 \cdot 10^{-3}$ μg. Fe in ml NH_3.

although a large amount of test material is used (20 g). The method suggested permits determination of down to $5 \cdot 10^{-6}$ % in a 10 g sample.

Experimental procedure. An aliquot of test material (up to 10 g) is placed in a 100 ml beaker and dissolved in 25 ml of ammonium tartrate solution (7.5 g of tartaric acid is dissolved in a small amount of water, 2-3 drops of phenol-red solution is added and the solution neutralized with ammonia; another 15-18 drops of the indicator solution is added and the whole diluted with water to 1 liter. Prior to use, 2 ml of a 3% solution of sodium thiosulfate is added per 100 ml of solution). The solution obtained is transferred to a 250 ml separating funnel. Into another separating funnel (control test) is added 25 ml of an ammonium tartrate solution. Next, to each of the funnels is added 15 ml of ascorbic acid and the solution immediately neutralized with ammonia using phenol red as indicator, 5 ml of 1-nitroso-2-naphthol solution (1 g/liter) is added and the solution diluted to approximately 150 ml with water and the whole mixed. After 40-50 min the solution is extracted twice with isoamyl alcohol, saturated beforehand with carbon dioxide (15, 10 ml), and the procedure adopted for constructing the calibration curve subsequently followed. In this case measurements should not be carried out later than one hour after commencing extraction.

Determination of iron in tartaric acid and its salts, as in other organic hydroxy acids, is carried out, as a rule, in the residue left after calcination [11]. This procedure is very long and contamination from metal vessels and from the air may occur. The method suggested permits determination of iron down to $1.25 \cdot 10^{-5}$ % without preliminary decomposition of the test preparation. In the procedure adopted use is made of a technique suggested earlier [12] for calculating the impurities in reagents during determination of traces in materials which are basic or acidic in character.

Experimental procedure. Two aliquots of tartaric acid differing in weight (e. g., 4.5 and 0.5 g) after dissolving in water, are transferred to 250 ml separating funnels. To each of the funnels is added 15 ml of ascorbic acid and a few drops of indicator, after neutralizing with ammonia, 5 ml of a solution of 1-nitroso-2-naphthol (1 g/liter) is added. The samples are then diluted with water to approximately 150 ml, the solutions are then thoroughly mixed, and after 40-50 min they are extracted twice with isoamyl alcohol (15, 10 ml). The procedure then followed is the same as that used for the construction of a calibration curve, and the first extract obtained from the large aliquot measured photometrically against the second. The iron content of 1 g of preparation (Z) is calculated by means of the formula:

$$Z = \frac{\Delta x - q(\Delta v)}{\Delta m},$$

where Δx is the iron content (in μg) corresponding to the optical-density reading, Δm is the difference in the two aliquots (in g), Δv is the difference in the volumes of ammonia used in neutralizing the two aliquots, and q is the iron content of 1 ml of ammonia established separately in a series of analyses (the measured volume of ammonia is evaporated in a beaker to dryness, the residue is dissolved in 20 ml of 0.05 M tartaric acid and the procedure used for constructing the calibration curve subsequently followed).

Results of checks on the methods of determining iron in the materials indicated are given in Tables 2 and 3.

In order to check on the reproducibility of the suggested methods, several determinations were made of iron in a sample of special-purity sodium iodide and in a sample of analytical-grade tartaric acid. The results are given in Table 4.

SUMMARY

A study has been made of the conditions for using the reaction of Fe^{2+} with 1-nitroso-2-naphthol for the extraction-photometric determination of traces of iron in highly pure materials.

The effect of a number of metal ions, as well as of citrate, tartrate, and phosphate ions on the reaction of iron with 1-nitroso-2-naphthol has been studied.

Methods have been developed for the determination of iron in sodium iodide for special purity and in tartaric acid, which permit determination of down to $5 \cdot 10^{-6}$ and $1.25 \cdot 10^{-5}$ % Fe, respectively.

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SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF NICKEL IN PURE INDIUM AND ALUMINUM

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Polarographic [1] or spectrographic [2, 3] methods are recommended for the determination of impurities in high-purity metals. Both methods require preliminary enrichment. Only one method is known which avoids the enrichment stage, this is the method by which nickel is determined in indium by means of dimethylglyoxime in the presence of an oxidizing agent. Unfortunately, this method has a low sensitivity and only permits determination of $2 \cdot 10^{-4}$ %; in addition, inference from copper is not excluded.

The aim of the work described here was to develop a method for determining nickel present as an impurity in the order of 10^{-6} %. The reagent used for nickel was α-furildioxime, which has a comparatively high sensitivity (ϵ = 19,000).

EXPERIMENTAL

Reagents and apparatus. Because of the necessity of determining less than microgram amounts of nickel all the reagents used had to be purified.

Nitric and hydrochloric acids, as well as ammonia, were purified by distillation. A quartz retort was used for distilling the nitric acid, while apparatus made from molybdenum glass was used for distilling the hydrochloric acid and the ammonia. As tests showed, one distillation was sufficient. The reagents used which were chemically pure grade materials — sodium tetraborate, tartaric acid, and citric acid — were tested for the presence of nickel in them, under the same conditions as those used for the determination of nickel in the test materials. A solution of α-furildioxime in chloroform was used as the reference solution.

Nickel was not detected in the reagents used by means of the reaction with α-furildioxime ($D < 0.01$).

The standard nickel solution was prepared by dissolving nickel sulfate in water acidified with sulfuric acid. Solutions containing 1 μg nickel per ml were prepared by appropriate dilution on the day they were to be used. Chloroform was purified from alcohol and carbonyl chloride by washing with a 5% alkali solution followed by distillation. Maximum increase in sensitivity during measurement of the light absorption of a solution was achieved by decreasing its volume to 5 ml and by increasing the working length of the cell to 5 cm. In view of the small volume of liquid a limiter with a slit of 5 mm was used.

The optical density was measured on a SF-4 spectrophotometer.

Factors affecting the sensitivity of the reaction between nickel and α-furildioxime. The reaction between nickel and α-furildioxime has been studied in detail by a number of authors [4-6] as applied to the determination of more than 5 μg of nickel. It is recommended that the compound obtained be extracted by organic solvents (usually chloroform) at a pH of 7.3-8.3. In connection with the necessity of determining 0.05-0.5 μg of nickel, a study was made of the relation between completeness of extraction and pH over a wider acidity range. The results which are given in Fig. 1 indicated that completeness of extraction of 0.5 μg of nickel is achieved in a more alkaline region (pH 8.5-9.4).

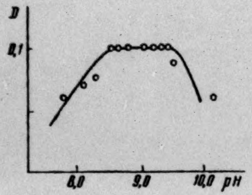

Fig. 1. Effect of the pH of the aqueous phase on the extractability of nickel.

In order to determine the value of the molar extinction coefficient, the complex nickel compound was isolated in the solid state; an aliquot of this material was then dissolved in chloroform. The molar extinction coefficient calculated from the light absorption of the chloroform solution proved to be 19,000 at 438 mμ.

In addition, it was established that during extraction of the complex compound with chloroform from a 25% aqueous-alcoholic solution, the molar extinction coefficient increases to 22,000. Acetone and dioxane exhibit the same effect. Chloroform solutions of nickel α-furildioximate conform to Beer's law down to 0.05 μg Ni in 5 ml (Fig. 2).

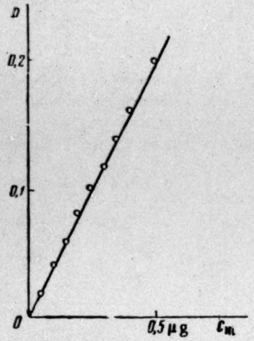

Fig. 2. Calibration curve for the determination of nickel with α-furildioxime; λ = 438 mμ; l = 5 cm; V = = 5 ml.

Effect of copper. Of the elements which accompany nickel, the one which has the greatest effect on its determination is copper, which forms with α-furildioxime a compound which is extracted by chloroform and also absorbs light at 438 mμ. It was found possible to eliminate interference on the part of copper by making use of differences in the stability of the ammines and α-furildioximates of copper and nickel. The complex compounds of copper and nickel were initially extracted with chloroform, the chloroform solutions were then washed with an ammonia solution 1:40. Results of these experiments are given in Table 1.

Determination of nickel in metallic indium and aluminum. Under the conditions used for determining nickel, indium and aluminum are precipitated as hydroxides. Accordingly tartaric and citric acids were added to the solutions; these acids do not affect the completeness of extraction of nickel α-furildioximate.

Determination of nickel in aluminum. One g of metallic aluminum is placed in a 100 ml quartz basin and dissolved in 10-15 ml of concentrated hydrochloric acid, the latter being added in small portions. The solution is evaporated almost to dryness and the residue transferred quantitatively by means of 30 ml of a 30% solution of sodium tartrate into a separating funnel, to which is then added 5 ml of a 0.1% solution of α-furildioxime and 25% alkali solution until the pH lies within the range 8.7-9.3 (checked by indicator paper).

After 2-3 min the complex compound which is formed is extracted twice with 2.5 ml lots of chloroform. The combined extracts are washed with 10 ml of ammonia (1:40). The volume of the chloroform solution of nickel α-furildioximate is then made up to 5 ml with chloroform and its optical density measured.

A solution of α-furildioxime in chloroform should be used as reference solution, this solution being obtained in the same way as the test solution. All the reagents used should be tested for any nickel present in them as impurity by the same method.

Results for the determination of nickel in aluminum in the presence and in the absence of copper are given in Tables 2 and 3. As is evident from these tables, nickel can be determined in metallic aluminum at a level of $5 \cdot 10^{-6}$% with a reproducibility of ± 20%; copper present in an amount which is one hundred times that of the nickel does not interfere.

TABLE 1

Determination of Ni in the Presence of Cu

Ni introduced, µg	Ratio, Cu: Ni	Ni found, µg	Error, %
0,50	10 : 1	0,49	— 2,0
0,20	25 : 1	0,19	— 5,0
0,10	50 : 1	0,11	+10,0
0,05	100 : 1	0,05	0,0
0,05	100 : 1	0,05	0,0
0,05	100 : 1	0,045	—10,0
0,05	100 : 1	0,06	+20,0

Determination of nickel in metallic indium. One g of the metal is placed in a 100 ml quartz basin and dissolved in 10 ml of concentrated nitric acid. The solution is evaporated almost to dryness, and the dry residue transferred quantitatively into a separating funnel by means of 20 ml of a 20% tartaric acid solution. Five ml of a 0.1% solution of α-furildioxime is then added followed by 10 ml of concentrated ammonia. The pH of the solution is checked using indicator paper and some additional ammonia added until the pH lies within the range 8.7-9.3. After 2-3 min the complex compound obtained is extracted twice with 2.5 ml lots of chloroform. The combined extracts are washed with 10 ml of ammonia (1: 40), and their volume adjusted to 5 ml with chloroform, the optical density is then measured as indicated above. During the extraction process a small amount of the precipitate of the double tartrate of indium and ammonium is formed; this precipitate, however, does not affect the results of the determination of nickel.

TABLE 2

Determination of Nickel in Metallic Aluminum (1 g sample)

Ni introduced		Ni found,	Error,	Ni introduced		Ni found,	Error,
µg	%	µg	%	µg	%	µg	%
0,50	$5\cdot10^{-5}$	0,51	+2,0	0,30	$3\cdot10^{-5}$	0,28	—5,6
0,50	$5\cdot10^{-5}$	0,49	—2,0	0,10	$1\cdot10^{-5}$	0,12	+5,0
0,50	$5\cdot10^{-5}$	0,52	+4,0	0,05	$5\cdot10^{-6}$	0,05	0,0
0,30	$3\cdot10^{-5}$	0,29	—3,3	0,05	$5\cdot10^{-6}$	0,06	+20,0
0,30	$3\cdot10^{-5}$	0,30	0,0	0,05	$5\cdot10^{-6}$	0,04	—20,0

TABLE 3

Determination of Nickel in Metallic Aluminum in the Presence of Copper (1 g sample)

Ni introduced µg	Ratio Ni: Cu	Ni found		Error, %	Ni introduced µg	Ratio Ni: Cu	Ni found		Error, %
		µg	%				µg	%	
0,50	1 : 10	0,52	$5\cdot10^{-5}$	+4,0	0,10	1 : 50	0,08	$1\cdot10^{-5}$	—20,0
0,40	1 : 12,5	0,42	$4\cdot10^{-5}$	+5,0	0,05	1 : 100	0,04	$5\cdot10^{-6}$	—20,0
0,30	1 : 16	0,29	$3\cdot10^{-5}$	—3,3	0,05	1 : 100	0,06	$5\cdot10^{-6}$	+20,0
0,20	1 : 25	0,23	$2\cdot10^{-5}$	+10,5					

TABLE 4

Determination of Traces of Nickel in Metallic Indium (1 g sample)

Ni introduced		Ni found,	Error,	Ni introduced		Ni found,	Error,
µg	%	µg	%	µg	%	µg	%
0,05	$5\cdot10^{-6}$	0,055	+10,0	0,05	$5\cdot10^{-6}$	0,040	—20,0
0,05	$5\cdot10^{-6}$	0,045	—10,0	0,05	$5\cdot10^{-6}$	0,050	0,0
0,05	$5\cdot10^{-6}$	0,045	—10,0	0,05	$5\cdot10^{-6}$	0,065	+25,0
0,05	$5\cdot10^{-6}$	0,050	0,0	0,10	$1\cdot10^{-5}$	0,110	+10,0
0,05	$5\cdot10^{-6}$	0,050	0,0	0,15	$1,5\cdot10^{-5}$	0,135	—10,0
0,05	$5\cdot10^{-6}$	0,060	+20,0				

TABLE 5

Determination of Nickel in Indium in the Presence of Copper (0.5 g sample)

Ni introduced, μg	Ratio Ni : Cu	Ni found		Error, %	Ni introduced, μg	Ratio Ni : Cu	Ni found		Error, %
		μg	%				μg	%	
0,50	1 : 10	0,49	$1 \cdot 10^{-4}$	−2,0	0,15	1 : 33	0,14	$3 \cdot 10^{-5}$	−6,6
0,25	1 : 20	0,21	$5 \cdot 10^{-5}$	+4,0	0,10	1 : 50	0,11	$2 \cdot 10^{-5}$	+11,0
0,20	1 : 25	0,18	$4 \cdot 10^{-5}$	−10,0	0,05	1 : 100	0,06	$1 \cdot 10^{-5}$	−20,0

Tables 4 and 5 contain results obtained during the determination of nickel in metallic indium in the presence and in the absence of copper. It follows from the results given in these tables that nickel can be determined in metallic indium at a level of $5 \cdot 10^{-6}$% with a reproducibility of ±25%; copper present in an amount one hundred times that of nickel does not interfere with the determination.

SUMMARY

Conditions have been established for the spectrophotometric determination of small amounts of nickel – down to 0.05 μg – by means of α-furildioxime, in solutions of its pure salts and also in the presence of one hundred times its amount of copper, by using an extraction method.

A method has been developed for determining traces of nickel in metallic aluminum at a level of $5 \cdot 10^{-6}$% with a reproducibility of ±20%, and in metallic indium at a level of $5 \cdot 10^{-6}$% with a reproducibility of ±25%.

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DETERMINATION OF MICROCONTENTS OF SELENIUM IN ORES AND ROCKS

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In connection with the development of geochemical methods of prospecting for scattered ore deposits, the necessity has arisen of determining selenium not only in ores but also in enclosing rocks with a sensitivity of the order of $8 \cdot 10^{-5}$%. Current methods of determining small amounts of selenium in sulfide ores are based on measuring the optical density of elemental selenium sols [1, 2], and are applicable for selenium contents in the test rocks ranging from 0.001% upwards. The difficulty in developing a more sensitive method consists primarily in choosing a method for decomposing the samples. Current methods of decomposition, and of removing HNO_3 on heating acid solutions [1-6] cannot be used, since, at low selenium contents, even small losses of this element, because of its volatility, have a pronounced effect on the experimental results. For microgram amounts of selenium these losses can amount to 100% even in the absence of chlorides.

Very serious difficulties are also met during separation of microgram amounts of selenium. High sensitivity of the photometric finish itself is also desirable.

We have developed a method for the determination of selenium in ores and rocks which has a sensitivity of 10^{-4}%; it is based on the acid-oxidation decomposition of test material, separation of selenium with ferric hydroxide and a photometric finish.

The individual stages of the technique as applied to microgram amounts of selenium were studied as a preliminary; these included; reduction and photometric determination, concentration by coprecipitation with ferric hydroxide, and decomposition of test material.

Reduction and photometric determination. Ascorbic acid was used for reducing selenium to the elemental state. Reduction was effected in a hydrochloric acid medium in tubes which can be centrifuged.

In order to concentrate and separate the reduced colloidal selenium from solution, coprecipitation and centrifuging with barium sulfate was used. For this purpose, ammonium sulfate and a known amount of barium chloride solution were added to a colloidal solution of selenium contained in a tube. The $BaSO_4$ formed entrained the elemental selenium, and, after centrifuging, a precipitate of barium sulfate colored rose by the selenium settled out on the bottom of the tube. As our tests showed, it is sufficient to add 150-200 mg of $(NH_4)_2SO_4$ and 1 ml of a 10% solution of $BaCl_2$ to 10 ml of a colloidal selenium solution. Under such conditions selenium passed completely into the $BaSO_4$ precipitate. The color intensity of the precipitate is reproducible and is proportional to the selenium content of the solution. On this basis it proved possible to prepare a scale of standards for determining selenium. It is most convenient to use as a standard scale $BaSO_4$ precipitates containing 0, 10, 15, 20, and 30 μg of Se. At higher selenium contents the gradation in the color intensity is not sufficiently marked. The smallest amount of selenium which is clearly discernible is 2 μg.

TABLE 1

HCl concentration, N	Se taken, μg	Se found, μg
0,1	15	10
1,0	15	13
4,0	15	15
10,0	15	10

TABLE 2

Duration of reduction, min	Se taken, μg	Se found, μg
2	15	8
6	15	12
10	15	13
45	15	15

TABLE 3

Time after acidification, min	Se taken, μg	Se found, μg
3	15	7,5
6	15	9
11	15	11
20	15	12,5
40	15	15
60	15	15

Such an experimental technique, in the first case, is more sensitive than the method of observing the colors through the thickness of a solution because the selenium is concentrated in a small (about 0.1 g) compact precipitate. Secondly, the color of the test solution, in the given instance, does not interfere, since the color of the precipitate is observed through the bottom of the tube. Thirdly, an important advantage of this method is the fact that such a standard scale is stable for a long time, at least for several months.

Selenious acid is reduced by ascorbic acid in both hydrochloric and sulfuric acid solutions. In the cold, however, reduction proceeds very slowly. Heating hydrochloric and, particularly, sulfuric acid solutions of ascorbic acid leads to rapid decomposition of the latter. On the basis of a number of experiments it was found that maximum reduction occurs when the ascorbic acid is introduced into a hydrochloric acid solution of selenious acid heated beforehand to 60-80°.

In order to evaluate the results of a study on the effect of acidity on the efficiency of reduction, and on the time necessary for complete reduction of selenious acid, a standard scale was prepared as described above. Reduction was carried out in hot solutions in a medium of 4 N hydrochloric acid. Barium sulfate was precipitated one hour after addition of ascorbic acid. In Table 1 is shown the extent of reduction of selenium 30 min after addition of ascorbic acid, as a function of the hydrochloric acid content of the solution. In Table 2 are given results which show the degree of reduction of selenious acid in 4 N HCl as a function of time. These results are reproducible to an accuracy of ± 1 μg. As is evident from Tables 1 and 2, the optimum hydrochloric acid concentration for reducing selenium is 4 N. In such a solution selenium is completely reduced in 20-30 min. The drop in reduction efficiency in 10 N HCl is explained by the instability of ascorbic acid in strongly acid solutions; it is also possible that selenium is lost on heating. As experiments showed, under such conditions, quantitative reduction of tellurium also occurs in a hydrochloric acid medium; tellurium, like selenium, passes into the barium sulfate precipitate and interferes with determination of selenium. In addition, gold present in solution, which usually leads to complications during the photometric determination of selenium [1], is also reduced with selenium.

In order to remove selenium from tellurium and other possible impurities, we made use of the capacity of selenium to dissolve in a concentrated solution of sodium sulfite to form selenosulfate [7, 8], which is destroyed on acidification to liberate elemental selenium. In order to dissolve the selenium from the $BaSO_4$ precipitate it is sufficient to heat it on a water bath for 5-10 min with 10% Na_2SO_3 which is 0.25 M with respect to Na_2CO_3.

Decomposition of the selenosulfate to yield elemental selenium on acidifying the solution does not occur instantaneously, but requires a definite time. In order to establish the time required for complete liberation of selenium, an equal volume of concentrated hydrochloric acid was added to its sulfite solution, and, after the turbulent liberation of SO_2 had ceased, the tube plus solution was placed in hot water. After a definite time the barium sulfate was precipitated and centrifuged as described above.

It is clear from Table 3 that complete liberation of selenium from its sulfite solution is only achieved 40 min after addition of acid. The colloidal selenium isolated in this way, free from foreign impurities, can be centrifuged again with a $BaSO_4$ precipitate.

Concentration by coprecipitation with ferric hydroxide. As a basis of the method a technique suggested by Proshkovich and Faleev [6] was used, their technique is based on coprecipitation of selenious acid with ferric

TABLE 4

Test material	Weight of aliquot, g	Se determined in the aliquot, μg	Se added, μg	Total Se, μg	Se determined in the sample, %
Breccia rock 1	0.25	16	10	27	$6.4 \cdot 10^{-3}$
" " 2	2.0	28			$1.4 \cdot 10^{-3}$
Mineralized serpentite	5.0	4	10	14	$0.8 \cdot 10^{-4}$
Phyllite with pyrrhotine minerals	2.0	11			$5.5 \cdot 10^{-4}$
Phyllite with quartz-carbonate streaks	2.0	3			$1.5 \cdot 10^{-4}$

hydroxide at a pH of 5.2, which is achieved by means of zinc oxide. At this pH complete coprecipitation of selenium occurs. Under such conditions nickel and a large fraction of copper remain in solution. At the same time selenium is separated from nitrate ions. Experiments carried out with solutions of selenious acid showed that for iron contents of the solution ranging from 50 to 500 mg, coprecipitation is complete. The volume of the test solution (from 50 to 300 ml), and any alkali metal salts present in solution in amounts up to 0.1 g/ml have no effect on completeness of coprecipitation.

Decomposition of test material. In view of unavoidable losses of selenium on heating acid solutions, we examined the possibility of decomposing samples of test material by prolonged action of aqua regia in the cold.

The test material used was various sulfide ores and rocks containing different amounts of sulfide. From 0.2 to 5 g of the finely ground sample was covered with aqua regia and allowed to stand overnight. The selenium content of the solution obtained was then determined. In order to check on completeness of decomposition, the undissolved residue was again subjected to the prolonged (16-18 hours) action of aqua regia. No selenium was found in the solution obtained after the second treatment in any one of the eight experiments carried out.

Experimental procedure. From 0.5-5.0 g of finely ground test material was placed in a conical flask and moistened with water, 25 ml of aqua regia was then added and the whole left to stand overnight. The undissolved material was filtered off through a No. 4 glass crucible. The solution was diluted with water to 150-200 ml, and 100-200 mg of ferric iron in the form of a solution added (when the amount of iron already in the solution is not enough), the solution was neutralized, first with an alkali solution, and then with an aqueous suspension of zinc oxide, and the whole heated on a water bath until the precipitate had coagulated completely. The supernatant liquid was decanted. The ferric hydroxide precipitate was washed by decantation until the wash liquors gave a negative test for nitrate ions. The wash liquor was prepared by neutralizing 0.05-0.1 N H_2SO_4 with zinc oxide. The washed precipitate was transferred to a tube and centrifuged, after which it was dissolved in the minimum amount of concentrated HCl, 3.5-4 ml of the latter was added in excess, and the volume made up to 10 ml with water. Tube plus solution were heated on a water bath to 70-80°, dry ascorbic acid was then added until the iron was completely reduced, when a further 300-500 mg of ascorbic acid was added in excess. After 30-40 min, 150-200 mg of $(NH_4)_2SO_4$ and 1 ml of a 10% $BaCl_2$ solution were added to the solution. The whole was centrifuged. The precipitate was washed first with hydrochloric acid 1 : 1, and then with water. To the washed precipitate was added 2 ml of a 10% Na_2SO_3 solution containing 0.25 g-mole/liter of Na_2CO_3 and the mixture heated on a water bath for 10 min. After centrifuging, the solution was transferred to another tube. This operation was repeated twice. To the sulfite solution (or an aliquot of this solution) was added an equal volume of concentrated HCl and the tube placed in hot water. After 40-50 min a second precipitation was carried out and the $BaSO_4$ centrifuged. From the intensity of the rose color of the precipitate on the bottom of the tube, using the standard scale the selenium content was determined.

In order to prepare a standard scale, appropriate amounts of selenious acid were added to solutions containing 25 ml of aqua regia and 200-300 mg of ferric iron. The solutions were neutralized and ferric hydroxide precipitated; the procedure subsequently followed was the same as that described above.

In order to check that selenium is not lost during the decomposition stage and during the subsequent analytical procedure, experiments were carried out in which known amounts of a selenious acid solution were added to aliquots of test material. Results for the determination of selenium in several ores and rocks are given in Table 4.

As indicated above, the smallest amount of selenium which can be determined is 2 μg, which for an aliquot material of several grams is equivalent to a sensitivity of the order of 10^{-4}%. The size of the aliquot is limted by the iron content of the sample. When the iron content of the aliquot exceeds 500-600 mg, the operations of separating the hydroxide precipitate from the solution and further reduction are complicated.

The accuracy for the determination of selenium when the amount of the latter in an aliquot is less than ten micrograms is 20-30%; for higher selenium contents the error is of the order of 10%.

SUMMARY

A study has been made of the conditions for reducing microgram amounts of selenium by ascorbic acid in hydrochloric acid solutions.

A new method has been developed for the determination of selenium; it is based on coprecipitation and centrifuging of elemental selenium with barium sulfate, and comparing the color intensity of the precipitate obtained with standards.

For the determination of microamounts of selenium a method of decomposing ores and rocks with aqua regia in the cold is suggested.

The method developed permits determination of selenium in ores and rocks with a sensitivity of the order of 10^{-4}%.

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DETERMINATION OF FLUORINE IN METALLIC ZIRCONIUM BY MEANS OF A DISCHARGE IN A HOLLOW CATHODE

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A study carried out earlier on discharges in a hollow cathode under high temperature conditions [1], has enabled the reactions which occur to be used for the spectrographic determination of small amounts of fluorine in metallic zirconium. Methods have been published on the spectrographic determination of fluorine and other halogens in difficultly volatile samples, mainly oxides, using as a light source a discharge in a hollow cathode in a helium atmosphere [2-4]. Fluorine is determined on the basis of atomic "quasiresonance" lines lying in the red and near-infrared parts of the spectrum. The sensitivity of the method is $1 \cdot 10^{-4}$ % for an accuracy of ± 10-15%.

Experiments which we have carried out in order to establish the possibility of using a similar method for the determination of fluorine in metallic zirconium have shown that the sensitivity obtained in this case is low (about 0.01%). The following are probably the reasons for this low sensitivity. Firstly, it is quite possible that the atomic lines of fluorine which are difficult to excite are weakened (the excitation potential of the corresponding energy levels is about 15 ev), when an appreciable amount of the main element of the sample – zirconium – passes into the discharge zone, since the ionization potential of the ions of this element is comparatively low – 6.95 ev. Although at a current intensity of about 300 ma, the source temperature (about 1000°) is still not high enough for appreciable evaporation of the zirconium (the vapor pressure at 1500° is about $1 \cdot 10^{-5}$ mm Hg [5]), the discharge spectrum nevertheless contains fairly intense zirconium lines, presumably as a result of sputtering of the test material on the cathode. At high current densities evaporation of zirconium becomes an essential factor (the vapor pressure is 0.01 mm Hg at 2000° and is 0.1 mm at 2200°). Secondly, the low intensity of the atomic lines of fluorine may be determined by the occurrence of secondary reactions. It is known that fluorine, like the other halogens, readily reacts on heating with zirconium [6], the very stable zirconium fluoride being formed (heat of formation 445 kcal). If it is assumed that the fluorine contained in the zirconium participates in the discharge mainly in the form of its compound with zirconium, the low sensitivity of an analysis based on the atomic lines becomes quite understandable. But, in such a case, it should be possible to develop a satisfactory method for determining fluorine by using the molecular spectrum of the compound which is most stable under the discharge conditions. Such a technique has been successfully used for the determination of fluorine [7-11]. The fluorine contained in test material is converted into its compound with calcium, strontium or silicon, and the determination is carried out on the basis of the molecular band of CaF or SrF, or on the basis of the atomic lines of silicon.

We detected in the spectra of samples of metallic zirconium obtained by the electrolysis of fused fluoride salts of zirconium an intense molecular band with a violet tinge.* The wavelength of the edge of the band was 2274.5 A. A microphotogram of it is shown in Fig. 1. We were unable to find any published information on this band or its nature. Accordingly, a series of special experiments were carried out which enabled us to establish

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* We detected in the region 2300-2350 A two further molecular bands which presumably form, together with the band noted, a system of bands.

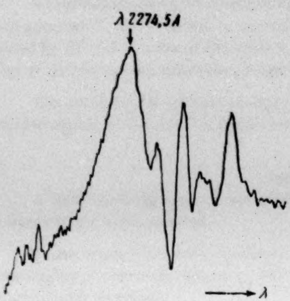

Fig. 1. Microphotogram of the band with an edge at λ 2274.5 A.

that the band detected actually belongs to a compound of fluorine with zirconium, its concentration being proportional to the fluorine concentration of the zirconium sample. We were unable to establish to which particular zirconium compound this molecular band belongs.

It was established that the band with an edge at λ 2274.5 A is present in the spectrum of a discharge in a hollow cathode in a helium atmosphere, both when graphite and metallic cathodes were used. The band indicated is also excited when zirconium dioxide containing fluorine in the form of TaF_5, NaF, or CaF_2 is placed in the cathode. The use of this band permits the determination of fluorine in zirconium dioxide with a sensitivity of $1 \cdot 10^{-3}\%$.

Preparation of zirconium samples containing known amounts of fluorine presents some difficulties. There are no reliable chemical methods for determining fluorine in metallic zirconium. It might be assumed that fluorine is contained in the metal in the form of potassium fluorozirconate, potassium fluoride, or zirconium fluoride. It is also possible that fluorine may be present as a compound with other elements found in metallic zirconium, but the probability of this being the case is low. Accordingly, in order to prepare standard samples, potassium fluorozirconate or KF was added to filings of zirconium iodide, in whose spectrum the band with an edge at λ 2274.5 A was absent. The filings were obtained by filing compact zirconium with a clean file. The filings were then sieved through a No. 0315 sieve demagnetized and washed with hydrochloric acid, distilled water, and alcohol. The mixture was ground in a tantalum mortar for 1.5 hours.

Filings of the test samples were prepared in the same way (without the grinding operation). In order to increase the reliability of the determination, aliquots of the standard samples and of the test samples were converted into brickettes by means of a press form (Fig. 2) and a laboratory hydraulic press at a pressure of 15 tons/cm².

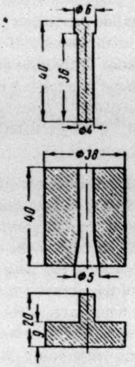

Fig. 2. Press form.

The setup described previously [1] with a hollow cathode was used for exciting the spectra of the test samples. The atomic lines of fluorine (6856.0 A and 7128.0 A) and the molecular band with an edge at λ 2274.5 A were photographed at the same timeon an ISP-51 spectrograph (with a UF-84 camera) and on an ISP-22 spectrograph. Photographic plates type "Infra-720" or "Paninfta" were used with the first apparatus, and "Spectrographic type III" or "Micro" were used in the second.

In experiments with brickettes of standard samples and test samples of electrolytic zirconium, the following facts were established:

1. The change in blackening of the edge λ 2274.5 A and of the atomic lines of fluorine with time is the same, for all the values of the discharge current tested (from 300 to 1200 ma). This holds true for both the standards and for the metal samples.

2. The intensity of the molecular band and of the atomic lines increases with increasing current intensity.

3. Conditions for determination on the basis of the edge at λ 2274.5 A are more favorable than those obtaining for the atomic lines of fluorine, since in the 7000 A region there is a strong continuous background

from the calcined sample on the cathode, while there is no background in the 2300 A region.

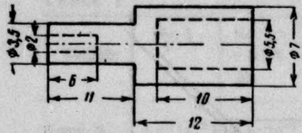

Fig. 3. Graphite cathode.

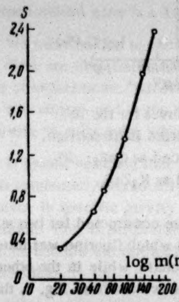

Fig. 4. The relation between the blackening of the band edge at λ 2274.5 A and the weight of the sample.

The sensitivity of the determination of fluorine based on the atomic lines is much lower than the sensitivity of determination based on the edge at λ 2274.5 A, and, as already mentioned, amounts to about $1 \cdot 10^{-2}$ %.

4. The most reproducible results, at a maximum intensity of the band edge at λ 2274.5 A, are obtained when the brickette is fused in a graphite cathode. The current intensity necessary for this depends (for constant cathode dimensions) on the size of sample, and also on the position of the brickette in the cathode. In accordance with data [12] on the increase in the intensity of ionic bombardment when the field in the cathode is not homogeneous, it was established that when the brickette lies on the lateral surface of the cathode, it melts at the lowest intensity of the discharge current. When a 50 mg sample is used in a cathode with the dimensions shown in Fig. 3, the brickette melts at a current intensity of 1000-1100 ma. In this case the fluorine is "burnt out" completely (according to the edge at λ 2274.5 A) in 60-90 sec for samples with a fluorine content of 0.1%.

5. Simultaneous recording of the potassium resonance lines λ 7664.9 and λ 7699.0 A on an ISP-51 spectrograph and of the edge at λ 2274.5 A made it possible to establish that for a sample of the original (not remelted) electrolytic zirconium, the blackening of the potassium line changes in accordance with the blackening of the band edge at λ 2274.5 A. This indicates that in the original zirconium, fluorine is present mainly as potassium fluorozirconate and KF.

In the case of remelted electrolytic zirconium this correspondence is not observed, and it is most probable that in such samples fluorine is present in the form of zirconium fluoride; this is also confirmed by a comparison of the corresponding thermodynamic constants [13].

6. The blackening of the band edge at 2274.5 A and the nature of these changes with time as a function of the helium pressure in the discharge tube change insignificantly within the pressure range studied (6-15 mm Hg).

7. The blackening of the edge at λ 2274.5 A strongly depends on the weight of sample (Fig. 4).

8. The sensitivity of the determination of fluorine based on the molecular band at λ 2274.5 A is $3 \cdot 10^{-4}$, for a sample weight of 50 mg. The sensitivity can be readily increased to $3\text{-}5 \cdot 10^{-5}$% by increasing the sample weight to 80-120 mg.

9. The optimum working conditions for determination of fluorine in the concentration range $3 \cdot 10^{-4}$ – $1 \cdot 10^{-2}$ % are as follows: sample weight, 50 mg; discharge current, 1100 ma; exposure, 60-90 sec; helium pressure, 8 mm Hg; photographic plates, "Spectrographic Type III" or "Micro"; slit width of the ISP-22 spectrograph, 30-35 μ. The working curve is constructed within the coordinates S, log C.

In order to be sure of the absence of systematic errors arising from variations in the behavior of fluorine in synthetic samples and in samples of metal, and as a result of third-component effects, we made a comparison of changes with time of the blackening of the analytical band with an edge at 2274.5 A for brickettes of synthetic mixtures containing fluorine in the form of potassium fluorozirconate and in the form of CaF_2, and for samples of electrolytic zirconium. The nature of the changes in blackening with time proved to be very close for all samples at a current intensity of 1100 ma (when the brickette was fused), while at lower current intensities, when the brickettes were not molten, appreciable differences were observed (Fig. 5).

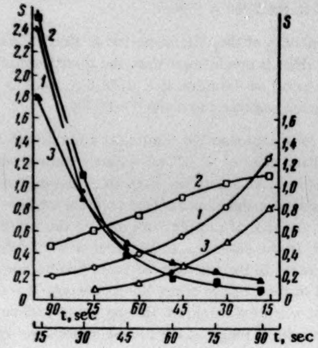

Fig. 5. Change of blackening of the edge at λ 2274.5 A with time. 1) Zr standard + K_2ZrF_6 (0.03% F); 2) Zr standard + CaF_2 (0.03% F); 3) sample of electrolytic zirconium Zr; △,□ – i = = 500 ma (the sample did not fuse); ●, ▲, ■ – i = 1100 ma (the sample fused).

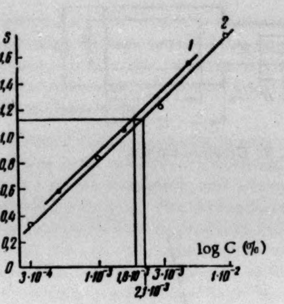

Fig. 6. Working curves for the determination of fluorine in zirconium. 1) Fluorine introduced as CaF_2; 2) fluorine introduced as K_2ZrF_6.

Two working curves were constructed for two series of standard samples, in one of which fluorine was introduced as potassium fluorozirconate, while in the other it was introduced as CaF_2. As is evident from Fig. 6, these curves have equal slopes and only suffer from a slight parallel displacement. Results obtained for synthetic mixtures of zirconium iodide with potassium fluorozirconate ($2 \cdot 10^{-3}$ % fluorine), by both working curves, coincide within the limits of the error of the method (see below). This fact enables one to make some conclusions on the role of tertiary components during the determination of fluorine on the basis of the edge of the molecular band at 2274.5 A. When fluorine is introduced in the form of potassium fluorozirconate, the standard mixtures contain graduated concentrations of potassium (approximately 1:1.5 relative to the fluorine content, in accordance with the stoichiometric ratio). When, under such conditions, the working curves almost coincide with curves constructed on the basis of standards not containing elements with low ionization potentials (standards with CaF_2), this indicates the absence of the effect of such elements on the intensity of the analytical band for contents of the third elements of about 0.01%. In order to establish how higher concentrations of elements with low ionization potentials affect the determination, a comparison was made of the analytical results obtained for fluorine for samples of electrolytic zirconium with the results for the same samples to which had been added 0.1% sodium as NaCl (Table 1). The original Na content of the sample was 0.01%, K << 0.01%.

Thus, when the sample contains high contents of the alkali metals, there is a danger that there will be an appreciable decrease in the results for the determination of fluorine, if measures are not taken to bring the composition of the standards close to that of the samples. This danger is, however, not so great when it is remembered that the alkali metal content does not exceed a few hundredths part of a percent.

Experiments with standards prepared by introducing fluorine in the form of CaF_2, which has been comparatively well studied, were useful from the point of view that they made it possible to make some conclusions regarding the behavior of fluorine during the analytical process as a function of the nature of the compound in which it is present in the sample. It is known that CaF_2 is a very stable compound (heat of formation 290.3 kcal [13]). When it is introduced into the light source molecular bands of CaF appear in the spectrum. Under the conditions which we used, however, the molecular bands of this compound were not present in the spectrograms of the series of standards to which CaF_2 had been added. It could be concluded from this that the side chemical reactions of fluorine with impurity elements present in the zirconium should not appreciably affect the results of fluorine determination. The results should not be distorted even in the case when fluorine is present in the zirconium in the form of compounds with impurity elements, as long as the stability of these compounds is not appreciably higher than that of CaF_2.

TABLE 1

Sample	No. 1	No. 1 + + 0.1% Na	ΔC, %
Found, %	$1.4 \cdot 10^{-3}$	$8.5 \cdot 10^{-4}$	−40

TABLE 2

Added, %	$2{,}0 \cdot 10^{-3}$ (CaF_2)	$2{,}0 \cdot 10^{-3}$ (K_2ZrF_6)	$5 \cdot 10^{-4}$ (K_2ZrF_6)
Found, %	$1{,}8 \cdot 10^{-3}$	$2{,}2 \cdot 10^{-3}$	$4{,}7 \cdot 10^{-4}$

The reproducibility of the results, evaluated from 30 spectrograms for zirconium samples containg $1.4 \cdot 10^{-3}$% fluorine, is characterized by a mean square error of a single determination of ±17% (relative). Thus, the experimental error is ± 10% (relative) for three parallel determinations.

We were unable to check on the reliability of our results by comparing them with those of other methods, since there are no reliable methods for the determination of fluorine in metallic zirconium. In Table 2 are given results of experiments "added—found", from which it is clear that even in those cases where fluorine is contained in the test sample and in the standards in the form of different compounds, the amounts of fluorine added are found with an error lying within the accuracy limits of the method.

It should be noted that the reproducibility for synthetic mixtures is somewhat lower than for metal samples. This is connected, presumably, with the unevenness of distribution of the salt introduced, following from the large difference in specific gravity and the degree of dispersion between it and the base material — filings of metallic zirconium. This is particularly the case when the standards are stored for a long time. Accordingly, bricketting should be carried out immediately after preparing the standards, and the standards should be stored in the form of brickettes.

When a zirconium sample containing a high content of fluorine is available, standard mixtures can be prepared by diluting it with zirconium iodide filings. The fluorine content of mixtures is established by analyzing them as carefully as possible on the basis of standards to which fluorine-containing salts have been added. When working with standards prepared by diluting a zirconium sample, the bricketting operation can be omitted.

When a triple-electrode discharge tube is used, it is possible to photograph the spectra and to calculate the results for 20-25 samples in a working day (3 parallel photographs for each sample). The preliminary operations require 7-10 min for each sample.

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SUMMARY

Taking as an example the determination of small amounts of fluorine in metallic zirconium the possibility has been demonstrated of making analytical use of the secondary chemical reactions which occur under the special conditions appertaining to a high-temperature discharge in a hollow cathode.

A highly sensitive spectrographic method has been developed for the determination of fluorine in metallic zirconium.

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CHEMICOSPECTROGRAPHIC DETERMINATION OF IMPURITIES IN LEAD

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At present, high-purity lead is being produced which contains 99.999% and upwards of this metal. It is known that impurities strongly affect the technological and physicochemical properties of the metal, and, accordingly, their amounts are limited by very firm specifications [1-5]. Determination of traces of many impurities by chemical methods presents considerable difficulties. In order to determine individual elements large aliquots of sample are necessary, in some instances even up to a kilogram [5-7].

Published spectrographic methods of analyzing lead provide for the determination of a series of impurities by exciting the spectrum in a spark or an arc between metallic electrodes, or in an arc between carbon electrodes filled with powdered lead compounds [8-15]. The sensitivity of direct spectrographic methods is not high enough for the analysis of high-purity lead.

A description is given below of a chemicospectrographic method developed in 1951 for the analysis of high-purity lead [16, 17]. The impurities are concentrated by separating the base element (lead) from a nitric acid solution in the form of sulfate. The concentrate of impurities obtained after evaporation of the decanted mother liquor in the form of $PbSO_4$ powder is subjected to spectrographic analysis. Twenty-four elements present as impurities are simultaneously determined with a sensitivity of $10^{-4} - 10^{-6}$%.

Precipitation of lead as the sulfate is fairly selective and permits its separation from numerous elements which form soluble sulfates [18-20]. It should be noted that in a number of standard methods of analyzing lead, use is made of the separation of $PbSO_4$ from impurities which are then determined in the mother liquor by chemical methods [6, 7].

The conditions under which $PbSO_4$ is precipitated in the method we have developed differ from the conditions adopted in classical methods of analysis. Partial precipitation is effected from hot, dilute nitric acid solutions. The nitric acid present enhances the solubility of lead sulfate, and this favors the growth of crystals and the self-purification of the precipitate. The $PbSO_4$ precipitate separated from the mother liquor is additionally subjected to recrystallization by heating with 6 N nitric acid. The conditions chosen completely eliminate loss of test elements with the $PbSO_4$ precipitate. In order to confirm the quantitative concentration of traces of elements in the mother liquor, it was essential to study phase distribution in a system consisting of one macrocomponent (lead) and a large number of microimpurities. In experiments with synthetic mixtures of salts under the conditions chosen for precipitation of $PbSO_4$, a study was made of the distribution between the solid and liquid phases of the following impurities: Na, Ca, Mg, Ba, Sr, Al, Ti, V, Cr, Mn, Mo, Co, Ni, Sb, Zn, Cd, Cu, Fe, Bi, Sn, Ag, Au, In, Tl, Te, As. To a nitric acid solution of spectrographically pure lead nitrate was added standard solutions of all the elements, and $PbSO_4$ precipitated with sulfuric acid. The lead sulfate separated from the mother liquor by decantation, was washed by boiling with nitric acid and subjected to spectrographic analysis. The decanted mother liquor, which was combined with the wash nitric acid, was evaporated to dryness and calcined. The concentrate of impurities obtained, the base of which is $PbSO_4$, was also analyzed spectrographically. In addition, the distribution of the individual elements between the phases were studied by means of the following radioactive isotopes: Ca^{45}, Cr^{51}, Mo^{99}, Fe^{59}, Co^{60}, Cd^{115}, In^{114}, Sb^{124}, $Sn^{113\ 123}$, Tl^{204}, Ag^{110}, Zn^{65}, Au^{198}. The activity of the concentrates and the precipitates obtained, as well as that of the corresponding standards, was measured on a type B-2 setup with a TS-17 torsion counter. In these experiments, in order to take into account the screening effect of the $PbSO_4$ precipitate, the same amount of lead sulfate as that present on the targets containing the sample was placed on the standard targets. A study was made of the effect of the nitric acidconcentration of the solution, the aging of the precipitate, excess Pb^{2+} or SO_4^{2-} ions, recrystallization of the $PbSO_4$ precipitate, and concentrations of the partitioned microcomponents. The content of each element in synthetic mixtures was varied from 10^{-1} to 10^{-6}%, and for certain elements, down to 10^{-7}% with respect to lead.

Experiments involving chemical and spectrographic analysis, and also radioactive indicators,gave results in agreement with each other; on the basis of these results the partition coefficients of the impurity elements between the solid and liquid phases were calculated. The following impurities remain almost completely (85-100%) in the aqueous phase: Na, Ca, Mg, Al, Ti, V, Cr, Mn, Mo, Co, Ni, Sb, Zn, Cd, Cu, Fe, Bi, Sn, Ag, In, Te, As. It should be pointed out that the elements indicated form sulfates which are not isomorphous with lead sulfate. As one might expect, strontium and barium,whose sulfates are isomorphous with $PbSO_4$, were coprecipitated with the lead sulfate.

Analytical procedure. An aliquot of lead weighing 10 g is dissolved in 45 ml of 6 N HNO_3 on heating, water is added to the solution obtained to bring the volume to 100 ml. $PbSO_4$ is precipitated by adding 35 ml of 3.6 N H_2SO_4 to the solution which has been heated to about 80°; the precipitate is then kept in the solution for three hours at room temperature. The mother liquor is removed by decantation and the lead sulfate recrystallized by heating with 40 ml of 6 N HNO_3 for two hours. The mother liquor which is combined with wash nitric acid is evaporated to dryness in a tared quartz basin. The powder thereby obtained, the base of which is $PbSO_4$, is calcined for 30 min at 550° and weighed. The enrichment coefficient of the impurities in the concentrate is calculated by means of the formula:

$$K = M/m \cdot 0{,}683$$

where M is the weight of lead taken (in g); m is the weight of concentrate (in g); 0.683 is the factor for converting $PbSO_4$ to Pb.

A sample in which chemical enrichment is not used is prepared by dissolving 1 g of lead or its compound in 20 ml of 6 N HNO_3. In order to convert the sample into the sulfate, the solution is diluted with water to 30 ml, and 6 ml of 18 N H_2SO_4 added. The solution plus precipitate is evaporated to dryness and calcined at 550°. In parallel to preparation of a sample for analysis, control experiments are carried out separately for concentrates and samples not enriched, using spectrographically pure lead sulfate.

All chemical operations are carried out in a vessel made of transparent quartz. The water and acids used are distilled beforehand in a quartz apparatus.

Spectrographic determination of impurities. The spectra of the chemical concentrate, the samples which have not been enriched, control experiments, and standard are photographed on the same photographic plate under identical conditions. The simultaneous photography of samples which have not been enriched is carried out for two reasons: firstly, those impurities which are not concentrated are determined in the sample which has not been enriched; secondly, the concentration range which can be encompassed can be extended appreciably using only one series of standards.

Spectrum excitation conditions: dc arc, 13 amp current; the lower electrode is a carbon rod with a crater 4.5 mm in diameter and 6 mm deep; the upper electrode is a rod sharpened to a cone. The amount of powder placed in the electrode crater is 100 mg. Exposure time 2.5 min; during this time complete evaporation of the sample in the arc discharge occurs. Photographic plates, spectrographic type II, spectrograph ISP-22, slit width 10 μ. A two-stage attenuator with relative transmission coefficients of 0.8 and 2.00 are fixed in front of the slit. In order to determine the impurities quantitatively, the method of constructing a calibration curve by means of standards within the coordinates log I, log C, using a calculating machine, is adopted. For the

TABLE 1

Analytical Lines and the Sensitivity of Determination of Impurities in Lead (the content of the elements is expressed as % wt. on lead)

Element and its analytical line	Sensitivity*		Element and its analytical line	Sensitivity*	
	not enriched	after concentration		not enriched	after concentration
Mg 2795,5	$2\cdot10^{-4}$	$5\cdot10^{-5}$	Ni 3050,8	$1\cdot10^{-3}$	$3\cdot10^{-5}$
Ca 4226,7	$1\cdot10^{-7}$	$5\cdot10^{-5}$	Cu 3247,5	$1\cdot10^{-4}$	$3\cdot10^{-6}$
Ba 2335,3 4934,1	$1\cdot10^{-3}$	—	Ag 3280,7	$3\cdot10^{-5}$	$1\cdot10^{-6}$
			Zn 2138,6	$3\cdot10^{-3}$	$1\cdot10^{-4}$
Al 3082,2	$3\cdot10^{-4}$	$5\cdot10^{-5}$	Cd 2288,0	$1\cdot10^{-4}$	$3\cdot10^{-6}$
Ti 3349,0	$1\cdot10^{-3}$	$3\cdot10^{-5}$	In 3256,1	$3\cdot10^{-4}$	$1\cdot10^{-5}$
V 3185,4	$2\cdot10^{-4}$	$6\cdot10^{-6}$	Sn 3175,0	$1\cdot10^{-3}$	$3\cdot10^{-5}$
Cr 4254,3	$3\cdot10^{-4}$	$1\cdot10^{-5}$	Sb 2598,1	$1\cdot10^{-2}$	$3\cdot10^{-4}$
Mo 3909,0	$1\cdot10^{-3}$	$3\cdot10^{-5}$	Bi 2898,0	$1\cdot10^{-3}$	$3\cdot10^{-5}$
Mn 2794,8	$3\cdot10^{-5}$	$1\cdot10^{-6}$	Te 2383,3	$5\cdot10^{-3}$	$2\cdot10^{-4}$
Fe 2719,0	$3\cdot10^{-4}$	$1\cdot10^{-4}$	As 2349,8	$5\cdot10^{-3}$	$2\cdot10^{-4}$
Co 3412,6	$6\cdot10^{-4}$	$2\cdot10^{-5}$	Au 2428,0	$5\cdot10^{-3}$	—

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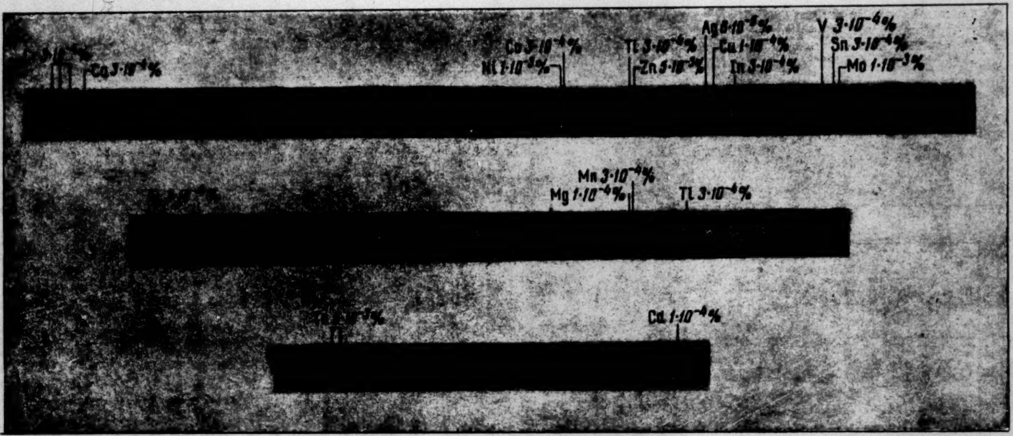
* The sensitivity for the determination of Mg, Ca, Al, and Fe is given after corrections for the control experiment.

TABLE 2

Checking the Method Developed on Synthetic Mixtures (as % wt. on lead)

Test element	Mixture I		Mixture II		Mixture III	
	added	found	added	found	added	found
Mg	$5\cdot10^{-5}$	$5,9\cdot10^{-5}$	$1\cdot10^{-2}$	$1\cdot10^{-2}$	$5\cdot10^{-5}$	$7,3\cdot10^{-5}$
Ca	$5\cdot10^{-4}$	$4\cdot10^{-4}$	$1\cdot10^{-2}$	$8\cdot10^{-1}$	$2\cdot10^{-4}$	$2,2\cdot10^{-4}$
Al	$5\cdot10^{-4}$	$4,2\cdot10^{-4}$	$1\cdot10^{-2}$	$1,2\cdot10^{-2}$	$2\cdot10^{-4}$	$4\cdot10^{-4}$
Ti	$5\cdot10^{-5}$	$3\cdot10^{-4}$	$3\cdot10^{-2}$	$3,6\cdot10^{-2}$	$2\cdot10^{-4}$	$4,8\cdot10^{-4}$
V	$5\cdot10^{-4}$	$4,4\cdot10^{-4}$	$3\cdot10^{-2}$	$3\cdot10^{-2}$	$2\cdot10^{-4}$	$2\cdot10^{-4}$
Cr	$5\cdot10^{-4}$	$4\cdot10^{-4}$	$1\cdot10^{-2}$	$1,3\cdot10^{-2}$	$2\cdot10^{-4}$	$1,8\cdot10^{-4}$
Mo	$5\cdot10^{-4}$	$4\cdot10^{-4}$	$1\cdot10^{-2}$	$1\cdot10^{-2}$	$2\cdot10^{-4}$	$2,5\cdot10^{-4}$
Mn	$5\cdot10^{-5}$	$4,7\cdot10^{-5}$	$1\cdot10^{-2}$	$1,2\cdot10^{-2}$	$5\cdot10^{-5}$	$4,2\cdot10^{-5}$
Fe	$5\cdot10^{-4}$	$3,6\cdot10^{-4}$	$3\cdot10^{-2}$	$3,5\cdot10^{-2}$	$2\cdot10^{-4}$	$2,2\cdot10^{-4}$
Co	$5\cdot10^{-4}$	$3,8\cdot10^{-4}$	$1\cdot10^{-3}$	$1,3\cdot10^{-3}$	$2\cdot10^{-4}$	$2,9\cdot10^{-4}$
Ni	$5\cdot10^{-4}$	$4,2\cdot10^{-4}$	$3\cdot10^{-3}$	$3\cdot10^{-3}$	$2\cdot10^{-4}$	$2,7\cdot10^{-4}$
Cu	$5\cdot10^{-5}$	$2\cdot10^{-5}$	$1\cdot10^{-2}$	$1,1\cdot10^{-2}$	$5\cdot10^{-5}$	$1\cdot10^{-4}$
Ag	$5\cdot10^{-5}$	$5,6\cdot10^{-5}$	$1\cdot10^{-4}$	$1,1\cdot10^{-4}$	$2\cdot10^{-4}$	$1,2\cdot10^{-4}$
Zn	$5\cdot10^{-3}$	$6,4\cdot10^{-1}$	$3\cdot10^{-2}$	$3,5\cdot10^{-2}$	$2\cdot10^{-4}$	$2,8\cdot10^{-4}$
Cd	$1\cdot10^{-4}$	$7\cdot10^{-5}$	$1\cdot10^{-2}$	$1,1\cdot10^{-2}$	$5\cdot10^{-5}$	$3\cdot10^{-5}$
In	$5\cdot10^{-5}$	$5\cdot10^{-5}$	$1\cdot10^{-2}$	$1\cdot10^{-2}$	$5\cdot10^{-5}$	$6,7\cdot10^{-5}$
Sn	$5\cdot10^{-4}$	$2,2\cdot10^{-4}$	$1\cdot10^{-2}$	$1\cdot10^{-2}$	$2\cdot10^{-4}$	$2,2\cdot10^{-4}$
Sb	$5\cdot10^{-3}$	$4,7\cdot10^{-1}$	$3\cdot10^{-1}$	$5,1\cdot10^{-1}$	$2\cdot10^{-3}$	$2,4\cdot10^{-7}$
Bi	$5\cdot10^{-4}$	$5,7\cdot10^{-4}$	$1\cdot10^{-2}$	$1,2\cdot10^{-2}$	—	—
Te	—	—	$1\cdot10^{-2}$	$8\cdot10^{-3}$	$1\cdot10^{-7}$	$7\cdot10^{-4}$
As	$1,6\cdot10^{-4}$	$1,5\cdot10^{-4}$	$5\cdot10^{-3}$	$7,5\cdot10^{-3}$	$5\cdot10^{-3}$	$7,7\cdot10^{-3}$
Au	$1\cdot10^{-4}$	$1,6\cdot10^{-4}$	$3\cdot10^{-4}$	$2,8\cdot10^{-4}$	—	—



Comparison of a spectrogram (a) for a sample of lead in the form of $PbSO_4$ with a spectrogram (b) for a concentrate of the impurities from the same lead sample on the same base for an enrichment coefficient K = 30.

analysis of the concentrate of impurities, the result obtained from the calibration curve is divided by the enrichment coefficient, in order to find the amount of a given impurity in the sample. Using one photographic plate the following elements are quantitatively determined separately: Ca, Mg, Al, Ti, V, Cr, Mn, Mo, Co, Ni, Sb, Zn, Cd, Cu, Fe, Bi, Sn, Ag, In, Te, As, Ba, Sr, Au. Determination of arsenic is carried out by means of a separate series of standards in view of the superposition of the analytical lines of Cd and As. Ba, Sr, and Au are only determined in samples which have not been enriched.

Thanks to the chemical enrichment of the impurities, the sensitivity of the method is increased 30-100 times as compared with the direct spectrographic method of analysis. Results on the sensitivity of the method are given in Table 1; the effect of enrichment of impurities on the increase in sensitivity is evident from the diagram. The accuracy and reproducibility of the method were checked on numerous synthetic mixtures which were prepared by adding all the elements indicated to a solution of spectrographically pure lead nitrate. The mixtures were analyzed by the method indicated above. The experimental accuracy depends on the concentration range, and differs for the various impurities. For impurities present in amounts of the order of 10^{-4}%, the accuracy is characterized by a relative error of ± 20% (Table 2).

The standards used for the spectrographic analysis were prepared on the basis of spectrographically pure lead sulfate by adding appropriate amounts of standard solutions of the elements.

SUMMARY

A chemicospectrographic method has been developed for the determination of impurities in lead and its compounds; it is based on the combination of a preliminary chemical concentration and subsequent spectrographic analysis.

The impurities are concentrated 30-100 times by removing lead from nitric acid solution in the form of its sulfate. The concentrate which is obtained on a lead sulfate base is subjected to spectrographic analysis simultaneously with a sample which has not been enriched, using the same standards.

A study has been made of the behavior of traces of elements, and of their distribution between liquid and solid phase under the experimental conditions. It has been shown that the elements: Na, Ca, Mg, Al, Ti, V, Cr, Mn, Mo, Co, Ni, Sb, Zn, Cd, Cu, Fe, Bi, Sn, Ag, In, Te, As are not coprecipitated over a wide concentration range (from 10^{-1} to 10^{-6}%) with the lead sulfate precipitate under the experimental conditions used.

The method developed permits the simultaneous determination of 24 elements with a sensitivity of 10^{-4} – 10^{-6}% with a relative error of ± 20%. The method can be used for controlling high-purity lead.

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ANALYSIS OF FLUOROORGANIC COMPOUNDS. SIMULTANEOUS MICRODETERMINATION OF FLUORINE, CARBON, AND HYDROGEN IN LOW-BOILING AND GASEOUS COMPOUNDS

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The present article is devoted to a description of the application of a method for the simultaneous determination of fluorine, carbon, and hydrogen [1-3] to the analysis of low-boiling and gaseous fluoroorganic compounds. The basic difficulties in the analysis of such materials are connected with taking samples and the introduction of samples into the combustion tube. Several methods have been described in the literature for the analysis of volatile liquids. In most cases a capillary containing an aliquot is sealed up and it is then opened either in the combustion tube itself by means of various gadgets, or it is opened immediately before being introduced into the tube [4-13]. Vessels of special design have also been suggested which are connected to the combustion tube and serve for breaking the ampoule containing the sample, and for mixing the vapors of the test material with oxygen [14-17]. As we have mentioned already [3], during the combustion of fluoroorganic liquids in a magnesium oxide layer, the use of glass capillaries for holding the sample is not desirable, since contamination of the magnesium oxide by lumps of fused glass can lead to damage of the apparatus and to incorrect experimental results. Accordingly, for the analysis of high-boiling liquids we used a quartz capillary, the end of which was left open. The weight of the capillary plus aliquot hardly changes even when the test liquid has a boiling point less than 100°.

Since, on taking samples in an open quartz capillary, combustion of a liquid is no more complicated than combustion of solid materials, it was interesting to check on the possibility of using such a capillary for the analysis of low-boiling liquids as well. As long ago as 1932, Pirsch [18] found that an aliquot of diethyl ether does not lose weight as long as the liquid layer in the capillary is separated from the surrounding medium by a few cubic millimeters of air found in the narrow end of the capillary. We established that the weight of various volatile liquids remained constant in a series of quartz capillaries the diameter of the open end of which was 0.2-0.3 mm. As can be seen from the results given in Table 1, thanks to the small diameter of the open end of the capillary and the small evaporation surface the losses following upon volatilization are comparatively small, are readily reproducible, and are constant with time.

In those cases where loss of the test material is appreciable, as for example, during the analysis of pentafluoropropane, knowing the change in weight of capillary plus sample per unit time, and the time which elapses between reading the balance and introducing the capillary plus test material into the combustion tube, it is possible to calculate how many micrograms it is necessary to subtract from the weight taken.

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* Deceased.

TABLE 1

Weighing of Volatile Materials in Open Capillaries

B. p. of material, °C	First reading, mg	Readings made after definite time intervals after the first reading, mg						Change in weight in one minute,* mg
		minutes						
		1	2	3	4	5	10	
78,4	3,195	3,195	3,195	3,195	3,195	3,195	3,192	0,000
56	1,225	1,220	1,218	1,212	1,210	1,205	1,188	—0,004
	9,210	9,208	9,200	9,192	9,188	9,182	9,155	—0,006
34,6	7,125	7,120	7,112	7,100	7,103	7,100	7,080	—0,004
	1,570	1,566	1,558	1,552	1,547	1,541	1,516	—0,005
27	3,430	3,420	3,412	3,401	3,990	3,980	3,970	—0,010
	5,160	5,151	5,139	5,130	5,120	5,110	5,101	—0,010
20	3,150	3,128	3,102	3,080	—	—	—	—0,023
	4,160	4,135	4,111	4,088	—	—	—	—0,024

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* Balance room temperature about 20°.

TABLE 2

Determination of Fluorine, Carbon, and Hydrogen in Volatile Materials, Samples on Which Were Taken in Open Capillaries

Test material	B. p.	C, %		H, %		F, %	
		found	difference	found	difference	found	difference
1-Ethylperfluoroisobutylene $C_6H_5F_7$	75°	34,36	+0,07	2,58	+0,18	63,70	+0,40
Calculated: C = 34.29%; H = 2.40%; F = 63.30%		34,41	+0,12	2,66	+0,26	63,40	+0,10
1-Bromo-2-hydroperfluoroisobutane C_4HBrF_8	56°	17,23	+0,13	0,39	+0,04	54,15	+0,06
		17,19	+0,09	0,38	+0,03	53,82	+0,27
Calculated: C = 17.10%; H = 0.35%; F = 54.09%							
3,3,3,1-Tetrafluoro-2-trifluoroisobutane $C_4H_3F_7$	40°	26,10	+0,02	1,66	+0,04	72,29	+0,01
		25,93	—0,10	1,53	—0,09	72,03	—0,20
Calculated: C = 26.08%; H = 1.62%; F = 72.28%							
1,2-Dihydroperfluoroisobutane $C_4H_2F_8$	35°	23,88	+0,12	1,15	+0,16	74,91	—0,33
		23,91	+0,15	1,06	+0,07	74,74	—0,50
Calculated: C = 23.76%; H = 0.99%; F = 75.24%							
3,3,3,2,1-Pentafluoropropane $C_4H_3F_5$	20°	26,96	+0,12	2,45	+0,22	70,41	—0,47
		26,96	+0,12	2.50	+0,27	70,57	—0,31
Calculated: C = 26.84%; H = 2.23%; F = 70.88%							

Note: All the analyses were carried out on samples of 4-8 mg.

Table 2 contains analytical results for liquid materials, aliquots of which were taken in open capillaries. It should be noted, however, that considerable skill is required on the part of the analyst when dealing with materials boiling at 20°, while for materials which are gaseous at room temperature, the method described above for taking samples cannot be, in general, used.

Samples of gaseous compounds can be taken either by volume – by means of a gas buret – or by weight – in a sealed glass capillary. The latter technique has the advantage that the percentage content of the elements in the aliquot can be calculated, without having to know the specific gravity of the material; however, it is only suitable for readily condensed gases which boil within the temperature range +20° to −45°. For reasons

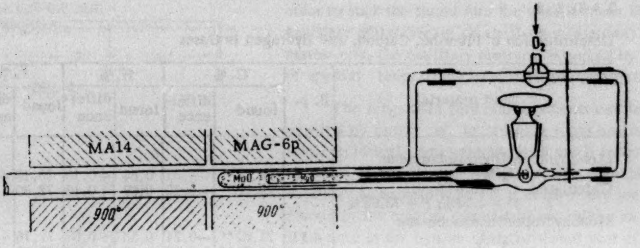
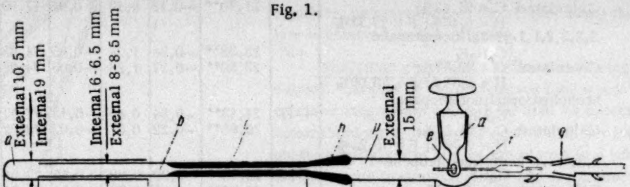

O2
MA14
MAG-6p
MoO3
900°
900°

Fig. 1.


External 10.5 mm
Internal 9 mm
Internal 6-6.5 mm
External 8-8.5 mm
External 15 mm
a
b
h
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d
90
110
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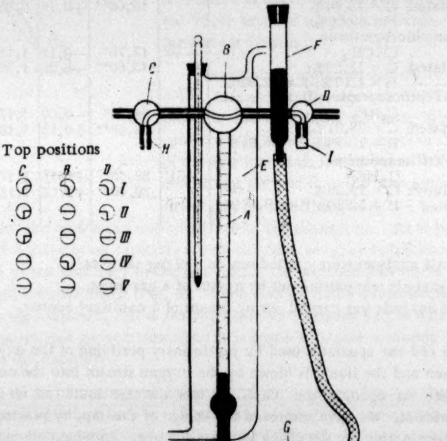
25
75
105

Fig. 2.


Top positions
C
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I
II
III
IV
V
A
B
C
D
E
F
G
H
I

Fig. 3.

reasons outlined before [3], a capillary containing an aliquot cannot be opened in the magnesium oxide layer, and, consequently, in this case it is necessary to break it inside the combustion tube.

Of the known methods used for this purpose we chose the "tap opener" suggested by Yu. N. Dagaevaya and K. I. Novozhilova. The end of the sealed capillary is placed in a hole in the barrel of a tap fitted between

TABLE 3

Determination of Fluorine, Carbon, and Hydrogen in Gases

Test material	B. p.	C, %		H, %		F, %	
		found	difference	found	difference	found	difference
Monohydroperfluoroisobutylene C_4HF_7 Calculated: C = 26.37% H = 0.54%; F = 73.02%	+18°	26,06**	−0,31	0,64	+0,10	73,13	+0,11
		26,08**	−0,29	0,67	+0,13	72,89	+0,13
Monohydroperfluoroisobutane C_4HF_9 Calculated: C = 21.83%; H = 0.46%; F = 77.71%	+13°	21,62**	−0,21	0,53	+0,07	77,76	+0,05
		21,70**	−0,13	0,42	+0,04	77,60	−0,11
3,3,3,2,1,1-Hexafluoropropane $C_3H_2F_6$ Calculated: C = 23.67%; H = 1.31%; F = 75.00%	+5°	23,33**	−0,34	1,28	−0,03	74,53	−0,47
		23,30**	−0,37	1,23	−0,08	74,93	−0,07
Monohydroperfluoropropane C_3HF_7 Calculated: C = 21.17%; H = 0.59%; F = 78.23%	−17°	21,13**	−0,04	0,46	−0,13	77,92	−0,31
		20,95**	−0,22	0,57	−0,02	78,52	+0,29
3,3,3,2,1-Pentafluoropropene-1 C_3HF_5 Calculated: C = 27.27%; H = 0.75%; F = 71.97%	−20°	26,98**	−0,29	0,90	+0,15	72,04	+0,07
		27,21**	−0,06	0,79	+0,04	71,71	−0,26
Hexafluoroazoxymethane $C_2F_6N_2O$ Calculated: C = 13.19% F = 62.63%	+8°	13,16*	−0,03	0	0	62,34	−0,29
		13,31**	+0,12	0,15	+0,15	62,36	−0,27
Trifluoronitromethane CF_3NO_2 Calculated: C = 10.44% F = 49.56%	−31,2°	10,43*	−0,01	0,07	+0,07	49,60	+0,14
		10,60**	+0,16	0,09	+0,09	49,39	−0,17
Difluorochloromethane $CHClF_2$ Calculated: C = 13.89%; H = 1.17%; F = 43.95%	−40°	13,78*	−0,11	1,10	−0,07	44,15	+0,20
		13,69**	−0,20	1,20	+0,03	43,95	0
3,3,3-Trifluoropropine-1 C_3HF_3 Calculated: C = 38.31% H = 1.07%; F = 60.61%	−46°	38,24*	−0,07	1,17	+0,10	60,52	−0,09
		38,46**	+0,15	1,16	+0,09	60,24	−0,37
1,1,2-Trifluoroethene C_2HF_3 Calculated: C = 29.28% H = 1.22%; F = 69.48%	−51°	29,45*	+0,17	1,17	−0,05	69,72	+0,24
		29,40**	+0,12	1,12	−0,10	69,30	−0,18

Note: All analyses were carried out on 4-9 mg samples.

* The analysis was carried out by means of a gas buret.

** The analysis was carried out by means of a capillary opener.

the combustion tube and the apparatus used for preliminary purifying of the oxygen (Fig. 1). On rotating the tap the capillary is broken and the liquid is blown by the oxygen stream into the combustion tube. This apparatus had the drawback that on opening the capillary tube the test liquid fell on the tap barrel and thereby led to possible losses of material. We have improved the design of this tap, by placing the tap in the top part of the apparatus, thereby eliminating the drawback indicated above. An added advantage of this design for the tap (Fig. 2) is that the capacity of the widened part of the capillary which is located under the tap coupling can be increased where it is necessary that the test materials be copiously diluted with oxygen for safe combustion.

Materials which boil at temperatures below +20° can also be analyzed by means of a gas buret (Fig. 3). Table 3 contains the results obtained during the analysis of gaseous materials, when various methods of taking samples were used.

Below is given a description of those stages in the analysis of volatile and gaseous compounds which differ from the corresponding stages in the analysis of solid materials described earlier [3].

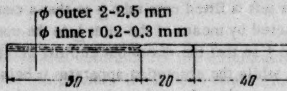

Fig. 4.

Analysis of volatile liquids boiling above 20°. Samples are taken in a quartz capillary (Fig. 4). In order to suck the liquid into the widened part of the capillary and to create an air stopper (blanket) in the narrow end, the capillary reservoir is cooled by means of special tongs which have cold compartments (Fig. 5).

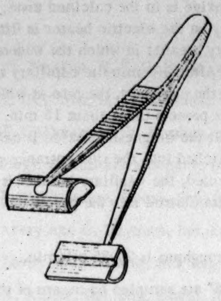

Fig. 5.

The tongs with cold compartments can be constructed by fusing on to ordinary tongs hollow, brass, semicylindrical compartments with small longitudinal channels on the clamping surfaces, which enable the capillary to be held reliably. Lumps of dry ice are placed in the cooling compartments. When an aliquot is located in the bottom of the widened part of the capillary, no movement of the aliquot along the capillary is observed during weighing.

Analytical procedure. Before introducing the aliquot, that part of the combustion tube where the calcined magnesium oxide to be used for successive determinations is located is cooled with dry ice. The quartz capillary plus aliquot are placed in a tube and is strewn with magnesium oxide and is introduced into the combustion tube so that the closed end of the tube is in the cooled zone. At the beginning of combustion, the cooled part of the tube is insulated from heat by means of an asbestos screen. Then, as the electric oven is moved forward, cooling is removed and the analysis is finished as usual by gradually moving the oven onto the whole layer of magnesium oxide. A combustion lasts about 20 min.

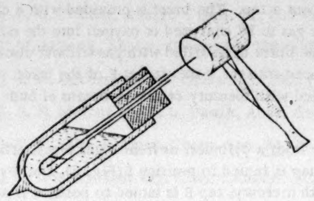

Fig. 6.

Analysis of materials boiling in the range +20 to −45°. Into a small Dewar vessel fixed in an inclined position, and containing a cooling mixture whose temperature is a few degrees lower than the boiling point of the test material, is introduced a sealed ampoule containing the test material, the ampoule itself being fitted into a rubber bung with two holes. After the ampoule has been immersed for 3-5 min, the drawn-out end which sticks out through the rubber bung is cut and broken. The widened part of a thick-walled glass capillary which has been weighed beforehand is gently warmed over a flame and the drawn-out part of the capillary in the test liquid; the widened part of the capillary is held by means of the tongs with the cooled compartments (Fig. 6). When enough liquid has collected in the capillary, its drawn-out end is withdrawn from the ampoule, and is sealed, while the widened part is still held in the cooled compartments of the tongs. Using the simple gadgets described it is possible to take a sample in such a way that it is all found in the widened part of the capillary.

The sample is introduced into the combustion tube by means of the capillary breaker (Fig. 2) which is a quartz tap d with a stopper which terminates in a loop e. On one side of the tap is fused a tube f through which the sealed capillary containing the sample is introduced, while on the other side is fused a widened tube p, which is connected via the capillary c with the tube b filled with magnesium oxide. Combustion of the test material occurs in tube b. The capillary breaker is connected to the combustion tube (Fig. 1) through a joint h which is not lubricated. It could be connected by means of a rubber bung, but this is not so convenient. The ground joint of the tap is lubricated with silicone grease.

In the case of these low-boiling liquids, approximately one and a half times more magnesium oxide is used than for the analysis of solid and high-boiling fluorides [3]. A blank run is made at the beginning of a working day. Magnesium oxide which has been pyrohydrolyzed beforehand is then strewn into tube a (Fig. 2), and from tube a into tube b. Tube a in which some magnesium oxide is left is fitted onto tube b so that a continuous MgO layer 9-10 cm long is obtained; the capillary breaker is connected by means of the joint h to the combustion tube and one of the capillaries containing a sample is placed in f so that the drawn-out end fits into the loop 3 in tap d. The joint g is connected to an oxygen supply, and, while the absorption apparatus is being weighed [3], the magnesium oxide is calcined, by moving the oven onto the tube and passing oxygen through the capillary breaker only (Fig. 1). The absorption apparatus is now connected to the combustion tube and the oven moved slightly in the direction of the oxygen stream, so that tube b containing the magnesium oxide sticks out from the oven a distance of 2 cm, while the rest of the magnesium oxide is in the calcined zone. In order to prevent heating of capillary c, an asbestos screen which presses tightly on the electric heater is fitted on the combustion tube; the aspirator tap is opened and that part of the capillary breaker in which the widened part of the capillary is located is cooled with dry ice, tube p is also cooled. After 2-3 min the capillary tip is broken by rotating the tap d, and the test material allowed to issue slowly from the capillary, the rate at which it issues being controlled by alternately applying and removing the cooling. This process takes about 15 min. When all the test material has come out of the capillary, cooling is stopped and all the magnesium oxide is calcined for 7-10 min. Next, by rotating the three-way tap, the oxygen stream is switched into the side entrance of the combustion tube, after a further 5-7 min the absorption apparatus is disconnected, the capillary breaker is switched off, all the magnesium oxide is strewn into the tube a, and the latter is transferred into the pyrohydrolysis tube as described previously [3].

Combustion as a whole takes about 25-30 min when the oxygen throughput is 20-25 ml/min.

Analysis of materials boiling below −45°. Gases boiling below −45° are sampled by means of the usual type of gas buret A (Fig. 3) having a volume of 2 ml. One filling of the buret is sufficient for 1-2 determinations. The buret is permanently connected into the setup used for carbon determination, between the capillary breaker and the gas-purifying system (Fig. 1). When the analyst is not working with a capillary breaker, it is necessary to have a similar following connecting quartz tube without a tap. The buret is provided with a crescent tap B by means of which it is possible either to introduce the gas to be analyzed or oxygen into the combustion tube, and with two additional taps C and D which allow the buret to be filled with gas without disconnecting it from the apparatus. Water from a thermostat is introduced into the water-jacket E of the buret. The zero reading of the buret is located at the tap B. The buret is filled with mercury or gas by means of bulb F and the screw clip G.

When sampling, the gas passes into the buret either directly from a cylinder, or from a gas pipet. The bulb F containing mercury is fixed in a position above tap B, the tap is turned to position I (Fig. 3), and, by opening clip G, the graduated part of the buret gradually filled with mercury; tap B is turned to position II and the clip closed. The gas inlet tube of the cylinder or a gas pipet is connected to the outlet H and gas passed through taps C, B, and D for 1/2 minute. During this operation the small drop of mercury which has entered into the opening in tap B during the operation of filling the buret is blown out by the gas stream into outlet I and is removed. The bulb F is then lowered, the clip G is opened slightly, and, by careful rotation of tap B into position I the gas is slowly let into the buret, after which tap B is turned back again into position II, and oxygen passed through all three taps (position III). During this operation the volume of the gas is read off at atmospheric pressure, and after setting the taps in position IV combustion is started.

At the beginning of a working day a blank run is carried out, oxygen being passed through the side entry of the combustion tube. While the buret is being filled with test gas, and after the blank run has been carried out, oxygen is passed through taps B, D, and C. The magnesium oxide is then prepared as indicated above; the weighed absorption apparatus is connected to the combustion tube and combustion of the gas commenced. For this purpose, bulb F containing mercury is fitted in a position above the levels of taps B, C, and D which are in position IV, and the screw-clip G is opened so that the gas issues from the buret into the combustion tube at the rate of about 0.2 ml/min. During this operation the oxygen is passed through the side inlet. When the requisite amount of gas has been passed into the apparatus, the taps are turned to position V for 10 min, and the gas supply line swept with oxygen. The oxygen is passed for a further 10 min into the side inlet of the combustion tube, after which combustion is complete. The total time taken for a combustion is 25-30 min, for an oxygen throughput of about 20-25 ml/min.

SUMMARY

A method is described for the simultaneous determination of fluorine, carbon, and hydrogen in volatile and gaseous compounds. It has been established that it is possible to take 4-9 mg samples of volatile liquids boiling at 20° and higher by means of quartz capillaries with open ends. A device is described which enables the capillaries containing samples to be opened outside the combustion tube, and a technique has been developed for taking samples of materials boiling in the range +20° to −45° in sealed capillaries.

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DETERMINATION OF PHENYL RADICALS IN SILICOORGANIC COMPOUNDS

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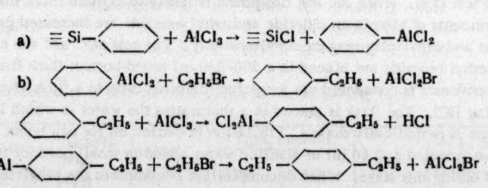
Methods for the analysis of silicoorganic compounds (SOC) have been described in detail [1, 2]. Physicochemical methods of determining radicals in SOC on the basis of their mass spectra [3, 4], and on the basis of their infrared and ultraviolet absorption spectra [5-9] have also been published. In view of the complexity of the methods indicated, however, they cannot always be used in laboratory practice. Until recently no chemical methods were known for the determination of radicals in SOC which would permit rapid and accurate control of the quality of the products obtained during the synthesis of high-molecular-weight SOC.

We have developed a new method for the quantitative determination of phenyl radicals in certain SOC; it is based on ethylation of phenyl-containing SOC by means of ethyl bromide in the presence of anhydrous aluminum chloride.

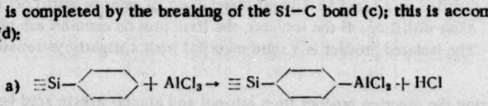
As our research showed, ethylation of SOC apparently proceeds according to two schemes:

Under the influence of $AlCl_3$ the Si–C bond is broken (a); this is accompanied by subsequent stepwise ethylation of the aluminoorganic compounds thereby obtained (b):



etc. Ethylation continues until hexaethylbenzene $C_6(C_2H_5)_6$ is formed.

Under the influence of $AlCl_3$ formation of aluminosilicoorganic compounds (a) ethylated with ethyl bromide occurs (b). The process is completed by the breaking of the Si–C bond (c); this is accompanied by formation of hexaethylbenzene (d):



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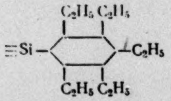
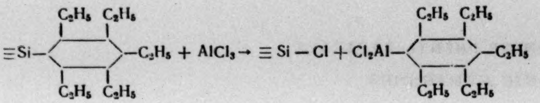
* A. A. Khvoshchevskaya and L. M. Kharchevnikova took part in the experimental work.

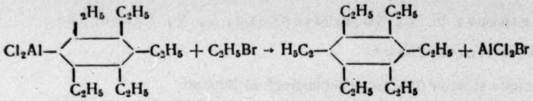
and so on right up to the formation of



c)



d)



On subsequent treatment of the reaction products with water, hexaethylbenzene containing other ethylated derivatives of benzene as impurities is obtained [10]. From the amount of the hexaethylbenzene formed it is possible to assess the content of phenyl groups in the original SOC. Hexaethylbenzene is characterized by a comparatively high average molecular weight and by its nonvolatility, which increase the experimental accuracy of the method. By observing constant ethylation conditions (concentration, temperature, and ethylation time) it is possible to obtain good reproducible results.

Our experiments on the ethylation of organic phenyl-containing compounds (benzene, diphenyl, toluene, etc.) with ethyl bromide in the presence of aluminum chloride have shown that it is also possible to use the ethylation reaction for the determination of benzene and its derivatives in organic compounds. Accordingly, the method suggested for the determination of phenyl groups may, probably, find use not only for SOC, but for other heteroorganic and organic compounds as well.

Our test materials were phenyltrichlorosilane, methylphenyldichlorosilane, polyphenylsiloxanes, polymethylphenylsiloxanes, and other SOC containing phenyl radicals directly connected to silicon atoms. Calculations of the original products were carried out on the basis of the following considerations. When the test SOC contains not more than one phenyl radical per structural unit of the original SOC, then 6-7 g (about 0.05 mole) of anhydrous aluminum chloride and 35-40 g of ethyl bromide (about 0.35 mole) are used for 2-2.5 g (about 0.01 mole) of the test SOC. When the test compound is likely to contain more than one phenyl radical per structural unit, the amounts of aluminum chloride and ethyl bromide are increased correspondingly. Ethyl bromide serves as solvent and ethylating reagent simultaneously. The test SOC and the calculated amounts of aluminum chloride and ethyl bromide are placed in a 200-250 ml round-bottom flask fitted with a ground-glass reflux condenser. The condenser is connected via a calcium chloride tube to a flask containing alkali solution which is used for absorbing HCl. The flask is placed in a thermostat the water in which is at a temperature of 30°. The reaction mixture is periodically shaken. Ethylation is carried on for two hours. At the end of this time the condenser is disconnected and 50 ml of distilled water added in small portions to the contents of the flask; the flask is cooled during this stage. When decomposition is complete the ethylated benzene derivatives are extracted with small portions (30-50 ml each) of diethyl ether, the amount of the latter taken being such that the total volume of the extract is 250 ml. The silicic acid precipitate is first separated by decantation and then by filtration. The extract obtained is washed with water until the water liquors give a neutral reaction, and the extract then distilled in a tared 50-100 ml Wurtz flask in order to distill off the solvents (diethyl ether and ethyl bromide). After distilling off the solvents, the flask plus its contents are placed in a vacuum desiccator containing P_2O_5. The isolated product is a solid material with a slightly yellowish color. The m. p. is 123-125°.

On recrystallizing the reaction product from ethanol and glacial acetic acid hexaethylbenzene is isolated and identified – white crystalline material (prisms), which is soluble in ether, benzene, toluene, in hot ethanol, and glacial acetic acid.

Found % C – 87.65; H – 12.35; mol. wt. 247; m. p. 126°
Calculated % C – 87.82; H – 12.35; mol. wt. 246; m. p. 126.5 (129°) [11].

The phenyl radical content is calculated by means of the formula:

$$C_6H_5 = \frac{a_e \cdot 77 \cdot 100}{a \cdot 246 \cdot K_e} = \frac{a_e \cdot 77 \cdot 100}{a \cdot 246 \cdot 0{,}91} = \frac{a_e \cdot 34{,}4}{a}\ \%,$$

where a is the weight of test material taken, in g; a_e is the amount of the ethylated product, in g; 77 is the mol. wt. of the phenyl group; and 246 is the mol. wt. of hexaethylbenzene.

K_e is the ethylation factor determined experimentally.

The ethylation factor is a correction to be applied for the purity of the ethylated product isolated and for the losses which occur during its isolation. The ethylation factor was determined by ethylating chemically pure phenyltrichlorosilane with a b. p. of 201°.

After carrying out the reaction,and the ethylated product has been brought to constant weight, the ethylation factor is calculated as: $K_e = M_e/M_h$ where M_h is the mol. wt. of hexaethylbenzene and M_e is the mol. wt. of the ethylated product:

$$M_e = \frac{M_{C_6H_5SiCl_3} a_e}{a},$$

where $M_{C_6H_5SiCl_3}$ is the mol. wt. of phenyltrichlorosilane.

In addition to phenyltrichlorosilane, the ethylation factor was also determined by means of methylphenyldichlorosilane, polyphenylsiloxane, and methylphenylpolysiloxane; the value thereby found for the ethylation factor was 0.91 ± 0.01.

Below are given elemental analyses which confirm the purity of the SOC used in our experiments.

$C_6H_5SiCl_3$ Found %: Si – 13.42; Cl – 50.40
Calculated %: Si – 13.26; Cl – 50.29
$C_7H_8SiCl_2$ Found %: Si – 14.51; Cl – 37.20
Calculated %: Si – 14.69; Cl – 37.05
$C_8H_{11}Si_2O_{2.5}$ Found %: C – 47.59; Si – 27.50; H – 6.05
Calculated %: C – 47.30; Si – 27.64; H – 5.51
C_7H_8SiO Found %: C – 61.48; Si – 20.49; H – 6.034
Calculated %: C – 61.73; Si – 20.71; H – 5.87

The phenyl-radical contents of test SOC are given in the following table.

Formula of the test product	Sample wt., a, g	Found a_e, g	C_6H_5 content		Error	M. p. of the ethylated product
			found	calc.		
$C_6H_5SiCl_3$	2,10	2,18	36,14	36,44	–0,30	123–125°
	2,28	2,44	36,77	36,44	+0,33	
$CH_3C_6H_5SiCl_2$	2,12	2,58	41,04	40,15	+0,89	123–124°
	2,18	2,52	39,73	40,15	–0,42	
$[(CH_3)_2SiOC_6H_5SiO_{1,5}]_x$	2,19	2,35	36,91	37,69	–0,78	122–124°
	2,01	2,25	38,50	37,69	+0,81	
$[CH_3C_6H_5SiO]_x$	2,00	3,34	57,44	56,62	+0,82	123–124°
	2,14	3,43	55,14	56,62	–1,42	

As is evident from the table, the results for the determination of phenyl radicals are reproducible to an accuracy of ± 1-1,5% (absolute).

SUMMARY

A new method has been developed for the quantitative determination of phenyl radicals in silicoorganic compounds; it is based on the interaction of phenyl-containing silicoorganic compounds with ethyl bromide in the presence of anhydrous aluminum chloride.

It has been established that the interaction indicated is accompanied by ethylation of phenyl-containing silicoorganic compounds with ethyl bromide, by decomposition of the ethylated reaction products, and by formation of ethylated benzene derivatives.

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SEPARATION OF THE LOWER ALIPHATIC ALDEHYDES AND KETONES BY PAPER CHROMATOGRAPHY, AND THEIR QUANTITATIVE DETERMINATION

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A method which has been developed for the identification and quantitative determination of the lower aliphatic alcohols ($C_1 - C_4$) by paper chromatography [1] has been successfully applied to the determination of the composition and amount of alcohols formed during the oxidation of n-butane at temperatures and pressures close to the critical values [2]. The problem which confronted us was to develop a technique for the qualitative and quantitative determination of carbonyl compounds in complex mixtures of the lower aliphatic aldehydes and ketones (formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, methyl ethyl ketone) which may be formed during the oxidation of n-butane. In order to solve this problem we used paper chromatographic separation of the corresponding 2,4-dinitrophenylhydrazones.

A large number of papers has been published on the chromatographic separation of carbonyl compounds by means of this method [3-10]. However, information on the separation of the mixtures of carbonyl compounds we are interested in is very sparse and is qualitative in nature [11, 12].

The possibility of carrying out quantitative determinations by means of paper chromatography has been examined earlier [13]. Experimental data on quantitative determination is only available for hydrazones of aromatic carbonyl compounds [14].

Separation of the 2,4-dinitrophenylhydrazones on ordinary chromatographic paper of the "Rapid Leningrad" type could not be achieved because of small differences in the properties of the hydrazones formed. In order to separate the mixture of aldehydes and ketones we are interested in, it is necessary to use paper which is hydrophobic in character; such paper is prepared by acetylation of the paper with acetic anhydride in a toluene solution [15-17].

The acetylating solution (1700 ml of toluene, 300 ml of acetic anhydride, and three drops of concentrated H_2SO_4) is poured into a 2 liter measuring cylinder, and sheets of chromatographic paper 120 × 300 mm^2 wound on a teflon spiral immersed in it. The measuring cylinder is placed in a thermostat, and at a temperature of 65-70° the reaction is complete in 8-10 hours. The paper is considered to be acetylated when a piece of it dissolves in chloroform. The paper is then washed in methanol until the odor of acetic acid is no longer detectable, and it is dried in air. The paper is soaked for 4-5 min in methanol prior to placing the test material on it; the methanol is used as the stationary phase; the mobile phase is hexane, heptane, or nonane. Hexane, heptane, or nonane is poured onto the bottom of the tank which is to be used for ascending chromatography (the efficiency of descending chromatography is equal to that of ascending chromatography) and a beaker containing methanol also placed on the bottom; the tank is hermetically sealed. In the course of 24 hours at a temperature of 20° the methanol saturates the mobile phase and the vessel is ready for use.

TABLE 1

R_f Values for the 2,4-Dinitrophenylhydrazones of Formaldehyde, Acetaldehyde, Propionaldehyde, Butyraldehyde, Acetone, Methyl Ethyl Ketone for Various Solvents on Various Batches of Acetylated Paper

Expt. No.	Paper batch	Mobile phase	R_f (20°, l = 300 mm)						
			formaldehyde	acetaldehyde	propionaldehyde	butyraldehyde	acetone	methyl ethyl ketone	2,4-dinitrophenylhydrazine
1	I	Hexane	0,26	0,33	0,62	0,90	0,52	0,75	0,00
2	I	Heptane	0,06	0,15	0,35	0,69	0,29	0,50	0,00
3	I	Heptane	0,07	0,20	0,36	0,60	0,23	0,48	0,00
4	I	Heptane	0,03	0,18	0,32	0,53	0,26	0,48	0,00
5	I	Nonane	0,06	0,16	0,30	0,54	0,25	0,39	0,00
6	II	Heptane	0,07	0,17	0,42	0,82	0,35	0,61	0,00
7	III	Heptane	0,04	0,10	0,24	0,46	0,19	0,33	0,00
8	III	Hexane	0,13	0,30	0,54	0,92	0,45	0,80	0,00
9	Published data [12]	Heptane	0,09	0,18	0,32	0,42	0,30	0,43	

The method was developed with the aid of synthetic mixtures of formaldehyde, aeetaldehyde, propionaldehyde, butyraldehyde, acetone, and methyl ethyl ketone. The hydrazones were prepared by interaction of the corresponding carbonyl compound with 2,4-dinitrophenylhydrazine in a methanol solution in a weakly acid medium, with subsequent heating at a temperature of 60° for one hour. Excess 2,4-dinitrophenylhydrazine, as shown below, does not interfere with the separation of the hydrazones. The solution containing the 2,4-dinitrophenylhydrazones is placed on a sheet of the acetylated paper in a thin strip or as a spot at a distance of 20 mm from the edge of the paper; the paper is then placed in the chromatographic tank. Good separation of the bands is achieved by placing amounts of the order of 10^{-6} g·mole of the 2,4-dinitrophenylhydrazones on the paper; larger amounts lead to overloading of the paper, and, accordingly, no separation is achieved.

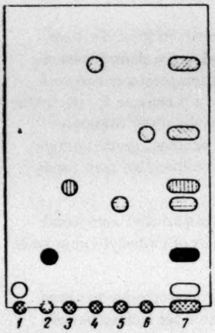

Fig. 1. Chromatogram of the 2,4-dinitrophenylhydrazones of the lower aliphatic aldehydes and ketones. 1) Formaldehyde; 2) acetaldehyde; 3) propionaldehyde; 4) butyraldehyde; 5) acetone; 6) methyl ethyl ketone; 7) a mixture of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, and methyl ethyl ketone. The excess of 2,4-dinitrophenylhydrazine remains on the starting line.

Complete separation of the compounds on a chromatogram at 20° is achieved in 3-4 hours; when the temperature is increased the rate of separation increases, but the definition of separation deteriorates. A typical chromatogram for a mixture of the 2,4-dinitrophenylhydrazones of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, and methyl ethyl ketone is shown in Fig. 1. The presence of other oxidation products (peroxides, alcohols, acids, esters) and water in amounts which are normally formed during the oxidation of hydrocarbons, does not interfere with the separation of the hydrazones. The R_f values obtained at 20° are given in Table 1. However, for strict identification of the test hydrazones, it is necessary to place on the same paper as that used for separating the hydrazones reference standards of the pure hydrazones of the corresponding carbonyl compounds, since on switching from one batch of acetylated paper to another, the R_f values vary strongly with the quality of the paper obtained by acetylation. The reproducibility of experiments carried out on the same batch of acetylated paper is quite satisfactory (see the R_f values for experiments 2 and 4 in Table 1).

When nonane, heptane, and hexane are used as the mobile phase, the R_f values (and, consequently, the differences between adjacent R_f values) increase with decreasing molecular weight of the hydrocarbon (Table 1). However, the efficiency of separation remains almost the same in all

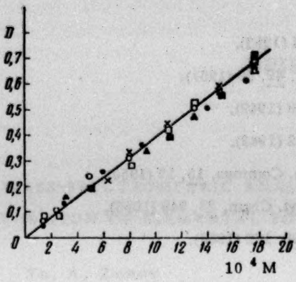

Fig. 2. Calibration curve for the quinoid forms of the 2,4-dinitrophenylhydrazones. ○) Formaldehyde; ●) acetaldehyde; □) propionaldehyde; ■) butyraldehyde; ×) acetone; ▲) methyl ethyl ketone.

TABLE 2

Separation and Quantitative Determination of Carbonyl Compounds from Their Synthetic Mixtures in Methanol

Compound	Taken in the mixture ($M \cdot 10^6$)	Found ($M \cdot 10^6$)	
		expt. no. 1	expt. no. 2
Formaldehyde	12.2	12.4	12.6
Acetaldehyde	10.6	10.8	11.0
Propionaldehyde	8.6	8.2	8.7
Butyraldehyde	6.4	6.0	6.8
Acetone	8.6	8.4	9.0
Methyl ethyl ketone	6.4	7.0	6.9

cases, since, at the same time, the diffuseness of the spots of the test hydrazones increases. The R_f value for 2,4-dinitrophenylhydrazine is always 0.00. After developing the chromatograms with a 5% solution of alcoholic alkali, all the hydrazones are colored a yellow-brown.

Quantitative determination of the 2,4-dinitrophenylhydrazones of the carbonyl compounds isolated from the mixtures was carried out on the basis of the light absorbed by the colored compounds with a quinoid structure which are formed on developing the chromatogram of the corresponding hydrazones. After development, the spot was cut out and the quinoid compounds of the 2,4-dinitrophenylhydrazones extracted with 5 ml of a 5% solution of KOH in methanol. The optical density of the solutions was measured on a SF-4 spectrophotometer or on a FÉK N-54 photocolorimeter at 480 mμ.

The amount of the carbonyl compounds is found from a calibration curve. We constructed such a calibration curve for formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, and methyl ethyl ketone at concentrations ranging from $1.5 \cdot 10^{-4}$ to $17.6 \cdot 10^{-4}$ M (Fig. 2). The calibration curves for all the compounds are almost the same and are straight lines, this is in agreement with published results [18].

Results of the separation and quantitative analysis of synthetic mixtures of the carbonyl compounds are given in Table 2.

The method suggested gives completely satisfactory results. The experimental error for the determination of aldehydes and ketones does not exceed 6%. Only in the case of methyl ethyl ketone does this error amount to 10%.

The author wishes to thank N. M. Émanuél' and Z. K. Maizus for valuable advice in carrying out this work.

SUMMARY

A method has been developed for the paper chromatographic separation and quantitative determination of the 2,4-dinitrophenylhydrazones of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, and methyl ethyl ketone. The presence of water and other products resulting from the oxidation of hydrocarbons does not interfere in the quantitative determination of the carbonyl compounds.

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BRIEF COMMUNICATIONS

THE MASS-SPECTROMETRIC ANALYSIS OF THE ISOTOPIC COMPOSITION OF ELEMENTAL BORON

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Determination of the isotopic composition of elemental boron is of practical importance. We have developed a technique for the isotopic analysis of boron by evaporating it from the ribbon evaporator of the ion source of a mass spectrometer, and subsequent ionization of the vapors obtained by electronic impact. A type MI-1301 mass spectrometer provided with an evaporating block was used in the course of the work. Measurement were carried out by a single-beam method. The ion source did not differ in constructional details from that described previously [1]. Bearing in mind the high boiling point of boron, tungsten foil 0.02 mm thick was used for making the evaporator; the shape of the evaporator was the same as that of a platinum evaporator [2].

About 0.1 mg of boron in the form of an alcoholic suspension was placed on the evaporator. This amount is sufficient for continuous work for 5-6 hours with completely satisfactory stability of the ion currents. Since the relationship between the temperature of the evaporator and the heating current of the block had not been determined beforehand, the requisite boron vapor pressure in the anode compartment of the ion source was achieved by regular [1] elevation of the evaporator temperature until an ion current of the highest intensity for the expected effective masses – about 1000-1500 mv – was obtained.

In the mass spectrum of the vapors above the boron, B^+ ions were discovered; these were used for calculating the isotopic composition of the test sample. Results for the analysis of elemental boron with a natural content of its isotopes are given in Table 1.

The boron was prepared from boric acid by reduction with magnesium [3]. The chemical purity of the product obtained in this way was not less than 86% with respect to the content of the main material. The boric acid used as an initial product for the preparation of elemental boron was also subjected to isotopic analysis by a method described in [2]. The results of these experiments are also given in Table 1.

Several samples of elemental boron enriched with the B^{10} isotope were analyzed by the method developed. These results are given in Table 2. As in the case of the analysis of boron with a natural content of its isotopes, these experiments were controlled by an analysis of the original product.

As is evident from Tables 1 and 2, the experimental results for the isotopic composition of elemental boron, obtained at different times are reproducible with a reasonable accuracy and agree very well with the results obtained during the analysis of boric acid.

In the course of an analysis, part of the boron is scattered on the details of the ion source of the mass spectrometer, and this affects the experimental accuracy of the isotopic composition of boron during the analysis of subsequent samples. In order to eliminate this effect it is sufficient to boil the anode compartment and the evaporator holder in a 3% solution of hydrogen peroxide, and then wash them with alcohol.

During the analyses attention was given to the evaporation process of boron from the ribbon evaporator. In the diagram a curve is shown which characterizes the change in the value of the ratio B^{11}/B^{10} during the

TABLE 1

Isotopic Composition of Boron in a Sample with a Natural Content of Its Isotopes

Date of measurement	B^{11}/B^{10} in the boron sample*	B^{11}/B^{10} in a sample of boric acid
5. I—1959	4,17±0,02	4,18±0,04
30. I—1959	4,18±0,01	4,16±0,03
04.II—1959	4,17±0,01	4,18±0,03
10.II—1959	4,17±0,01	4,18±0,02
16.II—1959	4,18±0,01	4,16±0,03

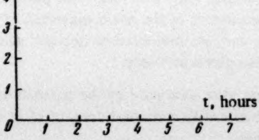
*Mean of 20-25 measurements.

TABLE 2

Isotopic Composition of Boron in Samples Enriched with B^{10}

Sample No.	B^{11}/B^{10} in boron*	B^{11}/B^{10} in boric acid
1	0.222 ± 0.001	0.222 ± 0.004
2	0.224 ± 0.004	0.226 ± 0.008
3	0.219 ± 0.002	0.222 ± 0.006
4	0.197 ± 0.002	0.200 ± 0.004
5	0.184 ± 0.003	—
6	0.207 ± 0.001	0.205 ± 0.005
7	0.168 ± 0.002	0.165 ± 0.003

*Mean of 20-25 measurements.



The relation between the value of the ratio B^{11}/B^{10} and time.

analysis. Four to five hours after the start of the evaporation process, the value of the ratio B^{11}/B^{10} starts to increase appreciably; this indicates that normal fractionation of the boron isotopes occurs during evaporation. This ratio is constant at the beginning of an experiment. Thus, the value of the isotopic fractionating effect during evaporation of boron is lower than the error of our measurements in the course of 4-5 hours from the beginning of an analysis, and does not affect the accuracy of the determination of the isotope ratio in boron. Results obtained at the end of an analysis cannot give the true ratio of the boron isotopes in the test sample.

SUMMARY

The method of evaporating from a ribbon-evaporator has been used during the mass-spectrometric isotopic analysis of elemental boron.

The isotopic composition of boron with natural and modified ratios of the isotopes has been measured. The results have been checked by comparing them with measurements of the isotopic composition of the boron in the starting material (H_3BO_3).

Evaporation of boron from the ribbon evaporator has been studied. It was found that during the evaporation of boron, normal fractionation of the isotopes of the latter is observed. The influence of the fractionating effects indicated on the accuracy of the determination of the isotopic composition of boron has been studied.

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TITRIMETRIC DETERMINATION OF NITRATES IN WATER

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The method described below for the determination of nitrates is based on their conversion into nitro derivatives of phenoldisulfonic acid, with subsequent titration of the latter with a solution of methylene blue in the presence of benzene, which quantitatively extracts the interaction products of the nitrophenyl derivatives and methylene blue. The low solubility of methylene blue picrate in water and its very good solubility in chloroform was noted by Rose in 1917 and was used by Bolliger [1] for developing a titrimetric method for the determination of picric acid. Bolliger [2] established that it is possible to determine the following dinitrophenols in the same way: 2,4-dinitrophenol, 2,6-dinitrophenol, 2,6-dinitroparacresol, 2,4-dinitroresorcinol, and 2,4-dinitro-α-naphthol; he noted, however that this method is not applicable to other nitrophenols.

During titration of methylene blue a compound of nitrophenol methylene blue is formed with a molar ratio of 1:1 of the components; on shaking, this compound immediately passes into the chloroform. When all the nitrophenol has reacted, the aqueous layer acquires a blue color. During this process the color changes as follows: yellow, yellow-pale greenish, yellow-green, green, and blue. A more clearly defined color change is observed with picric acid than with nitrophenols.

During determination of nitrates, after their conversion into the nitro derivatives, on titration with methylene blue using chloroform, the aqueous phase is colored green right from the beginning of titration; this color gradually increases, but the change from green to blue is difficult to establish. In order to increase the clarity of the color change, we tried various solvents and settled on benzene.

Extraction is incomplete in a neutral medium; the benzene layer remains almost colorless. In an alkaline medium the benzene layer is colored violet right from the beginning. The optimum medium for carrying out the reaction is a weakly alkaline medium which is 0.003-0.006 N with respect to NaOH added in excess after neutralization until the maximum yellow color is obtained. Under these conditions the reproducibility is completely satisfactory. NaOH concentrations which are 1-2 times greater or less than that indicated do not affect the results. When the NaOH concentration is five times greater, the results obtained are 5% too high, while for a concentration which is five times less the results obtained are 5% too low (Table 1).

The methylene blue solution is standardized against a solution containing a known concentration of NO_3^-. The color of the aqueous layer during titration with methylene blue in the presence of benzene changes as follows: greenish-yellow, green – the green is less intense than when chloroform is used – and then green-blue, and, finally blue. The change from green through green-blue to blue complicates determination of the end point of the titration.

From numerous experiments with concentrations differing by approximately five times from each other (Table 2), it follows that the bluish-green color of the aqueous layer which is observed up to 10-15% from the end point differs clearly from the blue color at the end point.

In order to establish the end point, separate titration of two similar samples should be carried out, in which the volume of reagent added to each sample differs by 0.1-0.2 ml. By using this technique it is possible to

TABLE 1

Solvent	NO_3^- taken, mg	NaOH concentration, N	Amount of 0.001 M methylene blue used, ml		
			to the green color	to the green-blue color	to the end point
$CHCl_3$	0,31	—	2,5	2,7	~3
$CHCl_3$	0,31	0,5—0,6	2,8	3,3	~4
$CHCl_3$	0,31	1,5—0,6	2,8	3,3	~4,2
C_6H_6	0,31	—	2,2	2,4	~3
C_6H_6	0,31	0,25—0,6	3,2	3,5	3,8±0,1—0,2
C_6H_6	0,31	0,5—0,6	3,3	3,5	3,8±0,1—0,2
C_6H_6	0,31	1,5—0,6	3,3	3,5	3,8±0,1—0,2
C_6H_6	0,155	0,1—0,6	1,3	1,6	1,8±0,1
C_6H_6	0,155	0,5—0,6	1,4	1,6	1,9±0,1
C_6H_6	0,155	2,5—0,6	1,4	1,7	2±0,1

TABLE 2

(1 ml of the methylene blue corresponds to 0.081 ± 0.004 mg NO_3^-)

NO_3^- taken, mg	0.6 N NaOH added, ml	0.001 M methylene blue solution used		
		to the green color	to the green+blue color	to the end point
0,31	0,5	3,3	3,5	3,8±0,1—0,2
0,31	0,5	3,3	3,5	3,8±0,1—0,2
0,155	0,5	1,4—1,5	1,6	1,9±0,05—0,1
0,155	0,5	1,4—1,5	1,6	1,9±0,05—0,1
0,0775	0,5	0,6—0,7	0,8	0,95±0,03—0,05
0,0775	0,5	0,3	0,4	0,475±0,025

TABLE 3

NO_3^- added, mg	NO_3^- found, mg
0,31	0,30
0,31	0,32
0,62	0,59
0,62	0,62

titrate with an accuracy of ± 5%. After some practice, when it is possible to decrease the difference between the volumes of reagent added to each sample, the experimental accuracy increases.

In order to check this method, determinations were carried out on samples of natural water free from nitrates but to which was added known amounts of NO_3^- (Table 3). The composition of the water* was as follows: NH_3 absent, NO_2^- absent. Oxidizability 9 mg of $KMnO_4$/liter; HCO_3 = 490 mg/liter; Cl^-, 12 mg/liter; SO_4^{2-}, 18 mg/liter; Ca^{2+}, 90 mg/liter; Mg^{2+}, 24 mg/liter.

Analytical procedure. Reagents. The phenoldisulfonic acid is prepared by heating 25 g of phenol crystals with 150 ml of H_2SO_4 sp.gr. 1.84 for six hours on a water bath under reflux. 0.001 M methylene blue solution. 0.01 M KNO_3 solution. Ag_2SO_4 solution (4.937 g/liter), 1 ml corresponds to 1 mg Cl^-.

The test water containing 0.1-1 mg NO_3^-, after precipitation of chlorides by addition of Ag_2SO_4,** is evaporated in a porcelain basin on a water bath. To the cooled precipitate is added 1 ml of phenoldisulfonic acid and the mixture stirred with a glass rod. It is allowed to stand for 10 min. 5-10 ml of distilled water is added. The solution is neutralized with 6 N NaOH by addition of the latter dropwise almost to the equivalence point. Addition of 0.6 N NaOH is continued until the liquid has a yellow color which does not increase in intensity on addition of a further drop of 0.6 N NaOH. The mixture is transferred to a 50 or 100 ml standard flask, the basin being washed out 3-4 times with distilled water. Into two similar cylindrical separating funnels or into two conical flasks fitted with glass stoppers are introduced equal volumes of the nitrophenolate solution. 0.5 ml of 0.6 N NaOH is added to each of them and the volume made up to 50-100 ml with distilled water. Benzene is added (the benzene and aqueous layers should have the same volume in both vessels).

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* The chlorine was removed with silver sulfate.

** For details of preparing the samples, see [3-4].

Both samples are titrated in parallel with 0.001 N methylene blue solution added in 0.1-0.2 ml lots and shaken vigorously after each addition. The aqueous layer initially has a yellow-greenish color and then becomes green, while the benzene layer has a violet color. Starting from the point at which the aqueous layer acquires an intense green color or a green with a blue tinge, titration is continued by addition of 0.1-0.2 ml more of the reagent to one sample than to the other. The end point is taken as that point at which the aqueous layer has a pure blue tinge. In the case of the sample to which less reagent has been added, the aqueous layer should have a bluish-greenish color, while in the case of the sample to which more reagent has been added the color of the aqueous layer should be blue.

The methylene blue solution is standardized against a standard KNO_3 solution.

Titration should be carried out at approximately the same rate.

SUMMARY

A method suggested for the determination of nitrates is based on their conversion to nitro derivatives of phenoldisulfonic acid, this is followed by titration with methylene blue solution in the presence of benzene which quantitatively extracts the interaction products of the nitrophenol derivative and methylene blue.

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THE USE OF THE HALOCHROMIC EFFECT IN QUANTITATIVE CHEMICAL ANALYSIS*

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The halochromic effect, i.e., the formation of intensely colored addition products by many organic compounds of the strong acids H_2SO_4, $HClO_4$, or inorganic compounds of the type $SnCl_4$, $AlCl_3$, $SbCl_3$, etc. has been studied by many authors [1-3]. The mechanism of these reactions reduces to an acid-base interaction of an organic dye with an inorganic reagent. Molecular compounds are formed by all organic reagents which contain the atomic groupings: $>C=O$, $-N=O$, $-N=N-$, $>C=N$, $>C=C<$, etc. having readily mobile π-electrons. The combination of the groups indicated with a system of aromatic type conjugated bonds, as well as the possibility of a change over into an ionic state, leads to the development of intense absorption bands in the visible part of the spectrum [4-6].

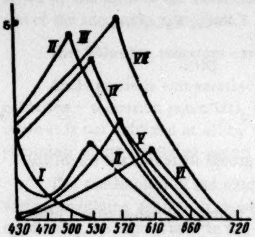

Fig. 1. Absorption curves of the halochromic compounds formed by dyes I-VII (Table 1) in H_2SO_4.

Some reactions in which halochromic compounds are formed have found analytical application, e.g., the method for the quantitative determination of $SnCl_2$ developed by Alimarin and Pevzner [7], the detection of carotene with concentrated sulfuric acid, the detection and semiquantitative determination of antimony with thymolphthalein [8], titration of hypochlorites in an acid medium by means of methyl orange [9], etc. Since, however, the appropriate reactions have not been studied sufficiently, the halochromic effect has not found wide application in quantitative inorganic analysis.

The present article is devoted to showing the possibility of using the halochromic compounds formed by dyes, as reagents for the quantitative determination of a number of oxidizing agents. In addition to dyes containing the atomic group $-N=N-$, it may be possible to use other dyes with different characteristic groups in chemical analysis.

In Fig. 1 are shown the absorption curves of the halochromic compounds of several azo dyes, while in Table 1 are given the values of the molar absorption coefficients of a number of azo dyes, their solubility in H_2SO_4, and their behavior toward certain oxidizing agents.

The molar absorption coefficients of the halochromic compounds of the azo dyes have high values, this ensures a high sensitivity for any analytical method based on their use, while the maximum of the absorption band may be located in almost any part of the visible spectrum, depending on the dye chosen. This fact is also very important in choosing an azo dye as an analytical reagent.

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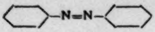
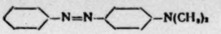
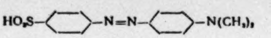
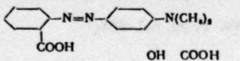
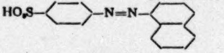
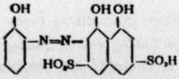
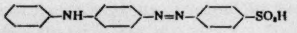
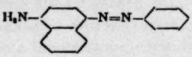
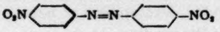
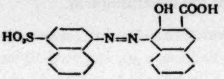
* A report given at the Eighth Mendeleev Conference on General and Applied Chemistry.

TABLE 1

Some Properties of Mono Azo Dyes

	Azo dye	λmax, mμ	ε × × 10^{-4}	Solubility in H_2SO_4, %	Oxidizing agent for the azo dye
I		430	2.1	>90	$KMnO_4$, $K_2Cr_2O_7$
II		530	2.2	$\geqslant 1$	$KMnO_4$, $K_2Cr_2O_7$, HVO_3, $Ce(SO_4)_2$
III		500	4.8	$\geqslant 1$	Ditto
IV		500	4.2	≥ 1	" "
V		470	3.2	>60	" "
VI		610	1.8	>60	" "
VII		570	5.2	$\geqslant 1$	" "
VIII		530	4.0	$\geqslant 1$	" "
IX		430	2.0	>95	$KMnO_4$, $K_2Cr_2O_7$
		570	3.6	>80	Ditto

The presence in the azo dye of hydroxyl, carboxyl (carbonyl), and amino groups increases the solubility of the dye in H_2SO_4, while the groups $-NO_2$ and $-SO_3H$ lower it.

The appearance in the azo dye of electron donating groups leads to a shift in the maximum to the long wave region of the spectrum.

From published data and from the author's experiments it follows that, azo dyes under the conditions leading to the formation of halochromic compounds (e.g. with H_2SO_4 and $HClO_4$) behave as reducing agents for MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-}, VO_3^-, Ce^{IV}, Cl_2, Br_2, hypochlorites, chlorites, the corresponding bromine compounds, and as oxidizing agents, e.g., for Sn^{II}, Ti^{III} [10].

Experiments on the possibility of using azo dyes for analytical purposes were carried out by two variants: photometric and titrimetric.*

The Photometric Variant. Equimolar (molar concentrations $2 \cdot 10^{-4}$) solutions (60% by volume with respect to H_2SO_4) of the halochromic compounds of the azo dyes and the corresponding solutions of the inorganic oxidizing agents were poured together in varying volume relationships: the volumes of the mixtures were always made up to a constant value (10 ml) with 60% sulfuric acid.

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* T. S. Zhigalkina participated in the experimental work.

In many cases the oxidation – reduction reactions proceeds rapidly; sometimes it lasts 30-60 minutes and even longer. The reaction rate depends on the nature of the dye, the value of the oxidation – reduction potential of the inorganic oxidizing agent, and on acid concentration; the nature of the acid also affects the oxidation – reduction potential of the oxidizing agent [13].

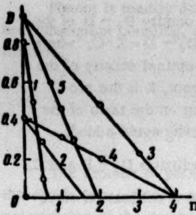


Fig. 2. The relation between the optical density of the halochromic compounds of the azo dye and the amount of oxidizing agent added [see Eqs. (1), (2), (3), (4), and (5)].

As soon as the optical density (D) of the mixture had become constant, it was measured on a photometer at λ_{max}. The experimental results are shown in Fig. 2.

It is clear from Fig. 2, that one volume (1 ml) of the azo dyes naphthyl red I, methyl orange III, V, and p-dimethylaminoazobenzene II, IV corresponds to the following volumes of solutions respectively: 0.66 ml $K_2Cr_2O_7$; 1.6 ml $KMnO_4$, 4.0 ml NH_4VO_3, 4.0 ml $Ce(SO_4)_2$, and 2.0 ml of Br_2 (bromine water).

A qualitative study of the reaction products showed that these could be nitrosubstituted diazo and azo components, mono and difunctional phenols, and their oxidation products – quinones; the composition of the products resulting from the oxidative break down of the azo dye depends on the nature of the oxidizing agent and the azo compound, and also on the time and reaction conditions.

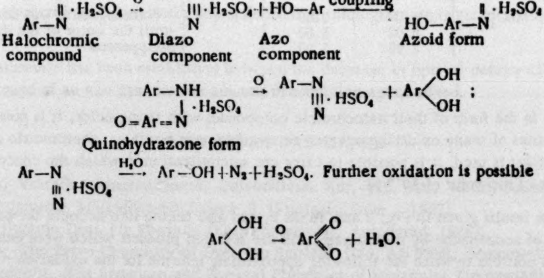
Whether or not complete destruction occurs of the products resulting from the oxidative break down of the dye by the continued action of an inorganic oxidizing agent with a high oxidation potential, is of no interest for the problem under consideration.

A decisive influence on the rate, the extent, and the possibility of the oxidation process is apparently shown by the ratio of the oxidation – reduction potentials of the azo dye which forms the halochromic compound, and of the inorganic compound.

The following reactions can be adduced as examples.

Azobenzene is comparatively readily oxidized by permanganate ($E_0 = 1.52$ v, where E_0 is the normal oxidation – reduction potential), it is oxidized with slightly greater difficulty by dichromate ($E_0 = 1.36$ v), while it is not oxidized at all by vanadate ($E_0 = 1.08$ volt). It should be noted that the oxidation – reduction potentials of the oxidizing agents indicated are strongly dependent on the acid concentration (see [12]).

The mechanism of the oxidation – reduction reaction, obviously, differs for the various azo dyes and the various oxidizing agents. It should be noted, however, that the oxidation of azobenzene by dichromate, can, apparently, be represented in the following way:



$$\begin{array}{c}Ar-N\\ \|\\ Ar-N\end{array}\cdot H_2SO_4 \xrightarrow{O} \begin{array}{c}Ar-N\\ |||\\ N\end{array}\cdot H_2SO_4 + HO-Ar \xrightarrow{\text{coupling}} \begin{array}{c}Ar-N\\ \|\\ HO-Ar-N\end{array}\cdot H_2SO_4 \rightarrow$$

Halochromic compound — Diazo component — Azo component — Azoid form

$$\begin{array}{c}Ar-NH\\ |\\ O=Ar=N\end{array}\cdot H_2SO_4 \xrightarrow{O} \begin{array}{c}Ar-N\\ |||\\ N\end{array}\cdot HSO_4 + Ar\begin{array}{l}OH\\ OH\end{array};$$

Quinohydrazone form

$$\begin{array}{c}Ar-N\\ |||\\ N\end{array}\cdot HSO_4 \xrightarrow{H_2O} Ar-OH + N_2 + H_2SO_4.$$ Further oxidation is possible

$$Ar\begin{array}{l}OH\\ OH\end{array} \xrightarrow{O} Ar\begin{array}{l}=O\\ =O\end{array} + H_2O.$$

It is known that during the oxidation of azobenzene by dichromate formation of p-hydroxyazobenzene occurs; the author has established that phenols (or quinone and phenol) are present.

Many facts are known [10] which indicate that the azo dye is in an azoid form in alkaline media and in a quinohydrazone form in acid media. In the scheme adduced above, we assumed that the p- and o-derivatives (with groups NR_2 and OH) of the azo dye participate in the reaction in the quinohydrazone form.

From an analytical point of view an important fact is that the decrease in optical density $D_0 - D$ of the halochromic compound is a linear function of the amount C of oxidizing agent added: $D_0 - D = K \cdot C$, where D_0 is the optical density of the original solution of the halochromic compound, D is the optical density of the solution of the halochromic compound after addition of a certain amount of oxidizing agent, K is the proportionality constant which determines the slope of the calibration curve and is dependent on the ratio of the stoichiometric coefficients in the equation of the reaction, and C is the amount of oxidizing agent added.

In this case the usual form of an ascending straight line is obtained within the coordinates $D_0 - D$ and C.

Nevertheless, any of the descending curves shown above (Fig. 2) can also be used as a calibration curve for the quantitative determination of the appropriate oxidizing agent. Using this relationship we have developed a method for the determination of vanadium in steels [1].

Titrimetric Variant. In those cases where the reaction proceeds rapidly, it is possible to titrate with the help of a solution of the halochromic compound of the azo dye, using it at the same time as the working material and as indicator.

In our work we used solutions of the dye and the oxidizing agent which had the same concentrations as in the photometric variant. The solvent was 60% (by volume) sulfuric acid.

Results for the titration of sulfuric acid solutions of the oxidizing agent by sulfuric acid solutions of the dye are given in Table 2.

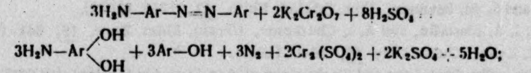
TABLE 2

Titration of Certain Oxidizing Agents With an Azo Dye

Order of titration	Oxidizing agent, ml	Dye, ml	Ratio: oxidizing agent/dye	Notes
$VO_3^- +$ Dye III	4.00 4.00 8.00	1.02 1.00 2.02	4 : 1	Titration was carried out to the appearance of the stable weak color of the dye (i.e., the color does not disappear)
$Ce^{IV} +$ Dye II	4.00 4.00 8.00	1.02 1.00 2.02	4 : 1	Ditto
$Cr_2O_7^{2-} +$ Dye V	2.00 2.00 4.00	3.02 3.02 4.04	2 : 3	
Methyl orange + MnO_4^-	4.00 8.02 7.98	2.50 5.00 5.00	8 : 5	Permanganate was added until the color of the dye disappeared

By using azo dyes in the form of their halochromic compounds with strong acids, it is possible, in principle, to determine small amounts of many oxidizing agents; two variants are possible: photometric and titrimetric. When the titrimetric variant is used, it is possible to carry out microtitration in which the concentration of the appropriate solutions are of the order of 10^{-4} M.

On the basis of the results given in Fig. 2 and Table 2, and also taking into account the scheme given above for the oxidation of azobenzene by dichromate, and the reaction products which were detected (qualitatively), it would seem possible to write the following approximate scheme for the oxidation–reduction reaction (the numbers given to the reactions correspond to the numbers on the straight lines in Fig. 2):



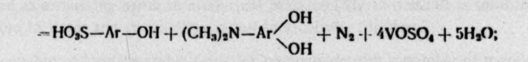
(1)

$$3H_2N-Ar-N=N-Ar + 2K_2Cr_2O_7 + 8H_2SO_4 =$$
$$3H_2N-Ar\genfrac{}{}{0pt}{}{OH}{OH} + 3Ar-OH + 3N_2 + 2Cr_2(SO_4)_2 + 2K_2SO_4 + 5H_2O;$$

Phenol is readily detected in the reaction mixture. After neutralization of excess H_2SO_4, diazotization and subsequent coupling, a dye develops which is proof of the presence of an aromatic amine in the reaction mixture.

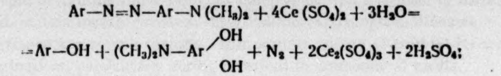
$$5Ar-N=N-Ar-N(CH_3)_2 + 8KMnO_4 + 12H_2SO_4 =$$
$$5Ar-OH + 5(CH_3)_2N-Ar-OH + 10HNO_2 + 8MnSO_4 + 4K_2SO_4 + 2H_2O. \quad (2)$$

The amount of permanganate added to the sulfuric acid solution of the dye, up to the point at which the dye is decolorized, corresponds to the stoichiometric coefficients (5 :8) given above; however, after decolorization of the dye, the permanganate added continues to be decolorized rapidly up to the point where the amount of it added is equivalent to 10 g-mole of HNO_2; after this point the permanganate is decolorized very slowly (presumably, a more profound decomposition of the organic material occurs). After the reaction mixture has been allowed to stand, nitrophenol could be detected in it (qualitatively); this fact indicates that nitration of the diazo component may have occurred.



(3)

$$HO_3S-Ar-N=N-Ar-N(CH_3)_2 + 4HVO_3 + 4H_2SO_4 =$$
$$= HO_3S-Ar-OH + (CH_3)_2N-Ar\genfrac{}{}{0pt}{}{OH}{OH} + N_2 + 4VOSO_4 + 5H_2O;$$



(4)

$$Ar-N=N-Ar-N(CH_3)_2 + 4Ce(SO_4)_2 + 3H_2O =$$
$$= Ar-OH + (CH_3)_2N-Ar\genfrac{}{}{0pt}{}{OH}{OH} + N_2 + 2Ce_2(SO_4)_3 + 2H_2SO_4;$$

$$HO_3S-Ar-N=N-Ar-N(CH_3)_2 + 2Br_2 = HO_3S-Ar-NBr_2 + Br_2N-Ar-N(CH_3)_2 \quad (5)$$

The reaction Eq. (5) was written in accordance with the stoichiometric coefficients obtained experimentally, and by taking into account the data given in [9].

It must be emphasized that the question regarding the composition and structure of the reaction products obtained during the oxidation – reduction breakdown of azo dyes requires further study.

SUMMARY

The possibility has been demonstrated of the wide use of azo dyes as analytical oxidation – reduction reagents for the photometric and titrimetric determination of microgram amounts of a number of oxidizing agents.

A linear relationship has been established between the decrease in optical density of a solution of the halochromic compound of an azo dye and the amount of oxidizing agent added.

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MASKING OF CATIONS BY MEANS OF UNITHIOL DURING COMPLEXONOMETRIC TITRATIONS

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Unithiol (sodium 2,3-dimercaptopropanesulfonate) is a white, finely crystalline material, which is readily soluble in water and is fairly stable in solution. It is used medically as an antidote for poisoning by many heavy metals [1]. Dimercaptopropanol (the British product lewisite) possesses similar properties. The latter has been used as a masking agent in analytical practice [2]. In contrast to unithiol, however, dimercaptopropanol is insoluble in water and its stability is low in alcoholic solutions.

Unithiol is capable of forming stable complex compounds with a number of metals. The complex compounds of unithiol with certain metals – sodium metallodimercaptopropanesulfonates – are more stable in some instances than the corresponding complexonates. This permits the use of unithiol for masking during complexonometric determinations, particularly during titrations in ammoniacal media.

As our studies have shown, unithiol displaces ethylenediaminetetracetic acid (EDTA) from its compounds with elements of the zinc, germanium, and arsenic subgroups. At the same time, the presence of unithiol does not interfere with the determination of calcium and magnesium ions and also of strontium and barium.* Accordingly, during the complexonometric titration of these cations, all the metals of the subgroups indicated (with the exception of germanium, on which no experiments have been carried out) can be reliably masked with unithiol. Results for the determination of ions of the second analytical group in the presence of cations of some of the heavy metals are presented in Tables 1 and 2.

TABLE 1

Determination of Calcium and Magnesium in the Presence of Zinc, Lead, and Bismuth

Masking ions, mg			Ca, mg			Mg, mg		
Zn	Pb	Bi	taken	found	error	taken	found	error
33	—	—	19.68	19.64	—0.04	—	—	—
33	—	—	—	—	—	12.28	12.33	+0.05
—	86	—	19.68	19.64	—0.04	—	—	—
—	86	—	—	—	—	12.28	12.28	0
—	—	15	19.68	19.73	+0.05	—	—	—
—	—	15	—	—	—	12.28	12.26	—0.02

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* Our work on this question has been sent for publication, and some of it has already been published in Zavodskaya Lab. 25, 1438 (1959), and Uch. Zap. Leningrad Gosud. Universiteta [in press].

In the same way it is possible to mask these cations during the complexonometric determination of lanthanum and, probably, other rare earths.

The complex compounds of unithiol with the elements of the zinc, germanium, and arsenic subgroups are not colored in an ammoniacal buffer medium. An exception is the yellow color of the complex of unithiol with bismuth and antimony. Accordingly, the permissible content of these cations in mixtures to be analyzed must be limited. At contents of these elements up to 20 mg in the solution being titrated, the color change of the indicator is clear enough at the end point.

TABLE 2

Determination of Strontium and Barium in the Presence of Zinc, Lead, and Bismuth

Masking ions, mg			Sr, mg			Ba, mg		
Zn	Pb	Bi	taken	found	error	taken	found	error
33	—	—	55.20	55.33	+0.13	—	—	—
33	—	—	—	—	—	74.49	74.04	—0.45
—	86	—	55.20	55.11	—0.09	—	—	—
—	86	—	—	—	—	74.49	74.49	0
—	—	15	55.20	55.11	—0.09	—	—	—
—	—	15	—	—	—	74.49	74.45	—0.04
—	—	6	5.687	5.700	+0.013	—	—	—
—	—	6	—	—	—	7.493	7.466	—0.027

Unithiol also forms complex compounds with silver, cobalt, copper, and iron. All these compounds are intensely colored in an ammoniacal medium and interfere with titration.

Unithiol interacts with manganese to form a brown-green colored compound. Manganese does not form a compound with sodium dimercaptopropane sulfonate when the unithiol is added to a solution which contains in addition, EDTA – Na, hydroxylamine, and triethanolamine. Accordingly, unithiol can also be used for the determination of manganese ions in mixtures with some other cations, in particular with zinc and lead (Table 3).

TABLE 3

Determination of Manganese in the Presence of Zinc or Lead

Mn, mg			Zn, mg			Pb, mg		
taken	found	error	taken	found	error	taken	found	error
16.73	16.69	—0.04	16.17	16.19	+0.02	—	—	—
16.73	16.74	+0.01	—	—	—	47.78	47.80	+0.02
8.828	8.844	+0.016	8.044	8.109	+0.065	—	—	—
8.828	8.818	—0.010	—	—	—	24.58	24.63	+0.05
1.653	1.655	+0.002	1.457	1.458	+0.001	—	—	—
1.653	1.651	—0.002	—	—	—	4.345	4.343	—0.002

Under such conditions, the determination is carried out as follows. The sum of the two cations is determined by direct titration with EDTA – Na, using eriochrome black as indicator, or by back titration with magnesium sulfate after adding EDTA – Na to the solution in a known excess. Unithiol is then added to the solution and the EDTA liberated titrated with magnesium sulfate.

Unithiol interacts with nickel to form a brown colored complex which is less stable than the corresponding complexonate. This permits separate determination of nickel in mixtures with cations which are masked by unithiol, e.g., with zinc or lead (Table 4). In this case, to the test solution, after addition of excess EDTA – Na solution and back titration with magnesium sulfate solution, unithiol solution is added, and the EDTA liberated again titrated with magnesium sulfate solution.

TABLE 4

Determination of Nickel in the Presence of Zinc or Lead

Ni, mg			Zn, mg			Pb, mg		
taken	found	error	taken	found	error	taken	found	error
14.60	14.56	−0.04	16.17	16.12	−0.05	—	—	—
14.60	14.62	+0.02	—	—	—	47.78	47.71	−0.07
7.124	7.106	−0.018	8.044	8.044	0	—	—	—
7.124	7.141	+0.017	—	—	—	24.58	24.67	+0.09
1.328	1.329	+0.001	1.457	1.455	−0.002	—	—	—
1.328	1.326	−0.002	—	—	—	4.345	4.354	+0.009

Sodium metallodimercaptopropanesulfonates are broken down by iodine and hydrogen peroxide. Accordingly, hydrogen peroxide can be used as an antireagent during masking with unithiol, so that it is possible to carry out successive complexonometric determinations of several cations in one aliquot (Table 5).

Unithiol can also be used as a masking reagent in combination with other masking agents, so that it is possible to increase the selectivity of complexonometric determinations.

TABLE 5

Successive Determinations of the Content of Alkaline Earth Elements in Zinc

Zn, mg			Ca, mg			Mg, mg		
taken	found	error	taken	found	error	taken	found	error
32.93	32.83	−0.10	20.28	20.34	+0.06	—	—	—
32.93	32.93	0	—	—	—	11.98	11.94	−0.04
15.307	15.323	+0.016	11.480	11.460	−0.020	—	—	—
15.307	15.356	+0.049	—	—	—	6.389	6.406	+0.017
2.575	2.582	+0.007	2.168	2.172	+0.004	—	—	—
2.575	2.566	−0.009	—	—	—	1.474	1.464	−0.010

It is important to note that the use of unithiol during masking of elements of the zinc subgroup enables one to do without potassium cyanide.

EXPERIMENTAL

1. Determination of Calcium and Magnesium Ions in the Presence of Zinc, Lead, and Bismuth Cations. To 10 ml of a 0.1 N solution of calcium chloride or magnesium chloride is added 10 ml of 0.1 N zinc or lead nitrate, or 10 ml of a bismuth nitrate solution in which the bismuth ion concentration is 1.5 g/liter. After adding to each of the samples 20 ml of a 2% aqueous solution of unithiol and 5-10 ml of an ammoniacal buffer solution with a pH of 10, the solution is diluted with distilled water to 100 ml, and some indicator − eriochrome black (a solid mixture of eriochrome black and sodium chloride in the proportion of 1 : 10) − added on a knife tip. The solution is finally titrated with 0.1 N EDTA-Na solution until the color of the solution changes from wine-red to blue.

2. Determination of Strontium and Barium Ions in the Presence of Zinc, Lead, and Bismuth Cations. To 10 ml of a 0.1 N solution of strontium nitrate or barium chloride is added 10 ml of a 0.1 N solution of zinc or lead nitrate. In this case to 10 ml of 0.1 N or 0.01 N solutions of these salts is added 10 ml of a solution of bismuth nitrate with a bismuth concentration of 1.5 g/liter or 0.6 g/liter. After adding to each of the samples 20 ml of a 2% aqueous solution of unithiol (in the case of 0.01 N solutions − 0.2% unithiol) and 5-10 ml of a 25% ammonia solution, the solution is diluted to 100 ml with distilled water. Next some indicator − cresolphthalein (a solid mixture of cresolphthalein, diamine green B, methyl red, and sodium chloride in the proportion 1 : 0.5 : 0.05 : 15) is added on a knife point, and the solution titrated with 0.1 N (in the case of 0.01 solutions − 0.01 N) EDTA − Na· solution until the color of the solution changes from violet to green.

3. Determination of Manganese Content in the Presence of Zinc or Lead Ions. To a mixture of 5 ml of a 0.1 N, 0.05 N, or 0.01 N solution of manganese sulfate and 5 ml of 0.1 N, 0.05 N, or 0.01 N lead nitrate solution or zinc sulfate solution is added 0.1-1.0 g of hydroxylamine, 1-5 ml of a 30% solution of triethanolamine, and 5-10 ml of an ammoniacal buffer solution with a pH of 10; some indicator – eriochrome black (a solid mixture of eriochrome black and sodium chloride in the proportion of 1:10) is added on a knife tip. After diluting the solution to 100 ml with distilled water the solution is titrated with 0.1 N, 0.05 N, or 0.01 N solutions respectively of EDTA – Na until the color changes from wine-red to blue. Ten ml of a 2%, 1%, or 0.2% solution, respectively, of unithiol is then added and the EDTA liberated titrated, depending on the concentration of the cations being determined, with a 0.1 N, 0.05 N, or 0.01 N solution of magnesium sulfate until the color of the indicator changes from blue to a dirty red.

4. Determination of Nickel in the Presence of Zinc or Lead Ions. To a mixture of 5 ml of a 0.1 N, 0.05 N, or 0.01 N solution of nickel nitrate and 5 ml of a 0.1 N, 0.05 N, or 0.01 N solution of zinc sulfate or lead nitrate, is added 5-10 ml of an ammoniacal buffer solution with a pH of 10, 20 ml of 0.1 N, 0.05 N, or 0.01 N solution of EDTA – Na, respectively, some indicator – eriochrome black (a solid mixture of eriochrome black and sodium chloride in the proportion of 1:10) is then added on a knife tip. The solution is diluted to 100 ml with distilled water and titrated respectively with 0.1 N, 0.05 N, or 0.01 N magnesium sulfate until the color of the indicator changes from blue-violet to wine-red. Ten ml of a 2%, 1%, or 0.2% solution of unithiol, respectively, is added (depending on the concentration of the cations to be determined) and the EDTA liberated titrated with magnesium sulfate solution.

5. Successive Determinations of the Alkaline Earth Elements in Mixtures with Zinc Ions. To a mixture of 10 ml of a 0.1 N, 0.05 N, or 0.01 N solution of calcium sulfate or magnesium sulfate and 10 ml of a 0.1 N, 0.05 N, or 0.01 N solution of zinc sulfate is respectively added 20 ml of 2%, 1%, or 0.2% solution of unithiol, 5-10 ml of an ammoniacal buffer solution, pH 10, and eriochrome black (a solid mixture with sodium chloride in the proportion of 1:10) added on a knife tip. After diluting the solution to 100 ml with distilled water, it is titrated with 0.1 N, 0.05 N, or 0.01 N EDTA – Na solution – depending on the concentration of the ions to be determined – until the color changes from wine-red to blue. To the solution is then added 1-5 ml of a 30% solution of hydrogen peroxide and the liberated zinc ions titrated with EDTA – Na solution until the blue color appears.

It has been established in this way that it is possible to use unithiol in analytical chemistry, and methods have been developed for masking heavy metal ions by means of unithiol during the complexonometric titration of calcium, magnesium, strontium, barium, manganese, nickel, and lanthanum.

SUMMARY

Unithiol (sodium 2,3-dimercaptopropanesulfonate) is capable of forming complex compounds – sodium metallodimercaptopropanesulfonates – with many heavy metal ions. The complexes of unithiol with the elements of the zinc, germanium, and arsenic subgroups are more stable than the corresponding ethylenediaminetetracetates. Unithiol hardly reacts at all with ions of elements belonging to the second analytical group and with lanthanum. Unithiol can, therefore, be used for masking during the complexonometric determination of these ions in the presence of zinc, cadmium, mercury, lead, tin, arsenic, antimony, and bismuth. Unithiol does not displace nickel, or manganese (in a medium of hydroxylamine and triethanolamine) from their ethylenediaminetetracetate complexes, so that it is possible to determine these ions in the presence of metals which are masked by unithiol. Unithiol is readily soluble in water and is fairly stable in solution.

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SOME AZOXY COMPOUNDS AS REAGENTS FOR CATIONS

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Azoxy compounds are quite similar in structure and in certain properties to azo compounds and azomethines, among which are found a number of important analytical reagents. In this connection we thought it would be interesting to study the possibility of using azoxy compounds in analytical chemistry, in particular for the photometric determination of cations.

A comparative study of the qualitative reactions of 2,2'-dihydroxyazoxybenzene (I), 2,2'-dihydroxyazobenzene (II), and salicylidene-2-aminophenol (III) with 60 cations by method A (see the experimental section) indicated that 2,2'-dihydroxyazoxybenzene had the highest sensitivity.

While I at a pH of 14 in the presence of small amounts of pyridine gives a highly selective color reaction with copper only, II and III under these conditions give color reactions with copper, cobalt, and nickel. At pH 4 this difference is even more clearly manifested: reagent I gives a color reaction with copper only, while reagent II gives a reaction with copper, zinc, aluminum, gallium, vanadium, indium, manganese, cobalt, nickel, and palladium, and reagent III gives a reaction with copper, vanadium, manganese, cobalt, and palladium.

Some of the characteristics of the reactions of reagents I-III with copper are given in Table 1.

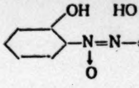
TABLE 1

Characteristics of Reagents I-III for Copper

Reagent	Maximum absorption, mμ		ε of reagent, ε of complex at λ	Visual sensitivity
	Reagents	Complex medium		
I	380	390	$2.5 \cdot 10^2$ $1.05 \cdot 10^4$ 480 mμ	0.25 μg Cu in 1 ml of the aqueous layer when the chloroform layer is 0.5 ml
II	420	420	$2.3 \cdot 10^2$ $1.7 \cdot 10^4$ 520 mμ	0.1 μg Cu in 1 ml of the aqueous layer when the chloroform layer is 0.5 ml
III	360	360	$8.7 \cdot 10^2$ $1.6 \cdot 10^4$ 420 mμ	0.15 μg Cu in 1 ml of the aqueous layer when the chloroform layer is 0.5 ml

As is evident, the increase in sensitivity observed on switching from the azo compounds tested and azomethine to the corresponding azoxy compound is accompanied by a drop in sensitivity. The fact indicated is, presumably, connected with the reduced complex formation tendency of the azoxy groups.

By including the azoxy group as an intermediate complex forming group in the system of a polydentate chelate former, we tried to find more effective reagents, in which the enhanced selective action of the azoxy group would be combined with an increase in complex formation as a result of the chelate effect. For this purpose, we synthesized and studied the following new compounds, containing in addition to o-hydroxyazoxy- or o-azo-azoxy groups, other chelate forming systems, they include: o-azoxyazo compounds from 2-amino-2'-hydroxy-5'-methylazoxybenzene (IV) and 2-naphthol (VI), H-acid (VII), R-salt (VIII), resorcinol (IX), 4,5-dimethylimidazole (X), the phenylhydrazone of benzoylformic acid,(XI) n-tolylhydroxylamine (XII), the α isomer of benzaldoxime (XIII),8-hydroxyquinoline-5-sulfonic acid (XIV), 2-naphthyliminodiacetic acid (XV), the azomethine from salicylaldehyde (XVI), and also o,o'-bisazoxy compounds from 2,2'-diaminoazoxybenzene (V), and 2-naphthol (XVII), p-cresol (XVIII), and H-acid (XIX).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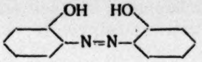
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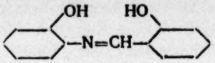
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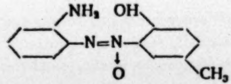
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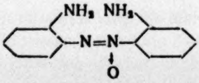
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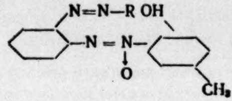
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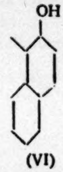
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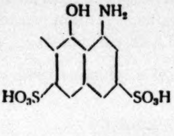
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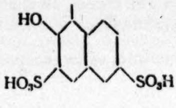
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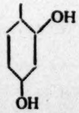
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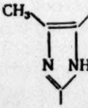
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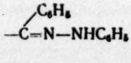
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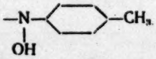
(XI)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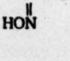
$-\underset{HON}{\overset{\|}{C}}-C_6H_5$

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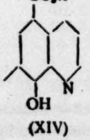
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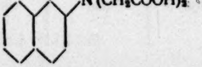
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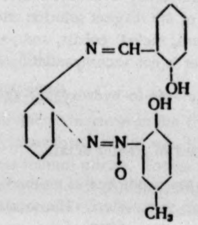

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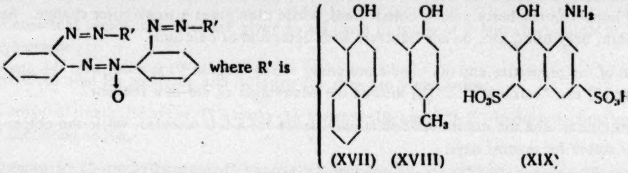

(XVII) (XVIII) (XIX)

Results of a study on the interactions of the synthesized compounds with 60 cations (Table 2) allow one to give the following general characteristics of the color reactions:

1. Reagents containing the o',o"-dihydroxy-o-azoazoxy group (reagents VI-IX), and also those similar in structure (X-XIII), as a rule, possess a fairly high selectivity. The most interesting of these reagents from the point of view of sensitivity and selectivity are reagents VI and VII.

TABLE 2

Characteristics of the Selectivity of the Reagents

Reagent	Ions which give color reactions (conditions :) (see experimental section)
VI	Cu. Co. Ca. Zn (pH 14)
VII	Cu, (pH 5—11); Mg, Zn, Bi, Fe^{II}, Co, Ni (pH 11); Pd (pH 1—5)
VIII	Cu, Ni, Pt$^{II, IV}$ (pH 1—11): Zn, Cd, La, Pd, Ir (pH 11); Sc, Co (pH 5—11)
IX	Cu, Ag, Co, Ni (pH 1—11); Zn (pH 5—11)
X	Cu, Ag, Zn, Mn (pH 5—11); Cd (pH 11); Co, Ni (pH 1—11); Pd (PH 1)
XI	Cu. Ca, Zn, Cd, Ga, Bi, Mo Mn, Co (pH 1—11)
XII	Cu, Co, Pd, (pH 1—11); Ca, Pb, (pH 11); Zn (pH 5—11); Ni (pH 1—5)
XIII	Cu, Co (pH 1=11); Zn, Cd (pH 5—11)
XIV	Cu, Ag, Ga (pH 11); Cd, Al, Sc, In, La, Fe^{II}, Ir (pH 5—11); Zr, Hf, Pb, Co (pH 1—11); Th (pH 1); Bi, Ni (pH 5); Pd, Pt$^{II, IV}$ (pH 1—5)
XV	Cu, Co, Pd, (pH 1—11); Ag, Zn, Cd, Mn (pH 11); V^{V}, Fe^{II} (pH 5); Cr^{III} (pH 1); Ni (pH 5—11)
XVI	Cu (pH 1—11); Zn (pH 11); V^{IV} (pH 1—5); Co (pH 5—11); Ni, Pd (pH 1)
XVII	Cu, Co (pH 5)
XVIII	Cu (pH 5—11)
XIX	Cu (pH 5—11); Co, Ni (pH 11); Pd (1—11)

2. Polydentate reagents containing, in addition to the o'-hydroxy-o-azoxyazo groups, other comparatively strong chelate forming systems – the partially isolated 8-hydroxyquinoline group* (reagent XIV) or the non-isolated group of iminodiacetic acid (reagent XV) – exhibit an appreciably lower selectivity in the color reactions with cations.

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* According to the classification suggested by one of us [1], this reagent belongs to the type of bisreagents with a common donor group.

3. Reagent XVI which contains the o,o'-dihydroxy-o-azoxyazomethine group, gives color reactions with 6 out of the 60 cations. The pale-yellow color of the reagent solution changes to red in the presence of copper, to orange in the presence of zinc, while vanadium, nickel, cobalt, and palladium lead to a weak color change. However, the enhanced selectivity of this reagent is not accompanied by high sensitivity.

4. Reagents (XVII-XIX) containing the o,o'-bis-(o-hydroxyazo)-azoxy group is distinguished by a very high selectivity.

The most promising reagents were examined in greater detail.

Reagent VI in an alkaline medium, under the conditions of method A, gives a selective reaction with calcium. The color change is from a rose-orange to colorless. The sensitivity of the visual reaction is 0.5 μg of calcium in 0.5 ml of the aqueous volume, when the volume of the carbon tetrachloride is 1 ml. For λ_{max} of the reagent of 510 mμ, $\epsilon = 1.815 \cdot 10^4$. In addition to the reaction with calcium, the reagent only gives a color reaction with copper (a raspberry color), cobalt (red), while zinc gives a weak color change. Barium, strontium, magnesium, beryllium, etc. do not interfere with detection of calcium.

A comparison of the properties and the conditions under which reagent VI is used, with the analytical data relating to murexide [2] and "calcion IREA" [3] showed the advantages of the new reagent.

1) When murexide is used the color obtained is only stable for a few minutes, while the colors given by the new reagent are stable for several days;

2) calcium can be determined by means of the new reagent in the presence of considerably larger amounts of salts (10-20 times) than is possible when "calcion IREA" is used.

Reagent VII in an alkaline medium (pH 10-11) gives a selective reaction with zinc. The color of the reagent solution changes from red to blue-violet. The sensitivity of the visual reaction is 0.25 μg zinc in 5 ml of solution. λ_{max} for the reagent is 560 mμ, while λ_{max} for the complex is 580 mμ; $\epsilon_{reagent}$ is $8.3 \cdot 10^3$ at 620 mμ, while $\epsilon_{complex}$ is $2.4 \cdot 10^4$ at 620 mμ. In addition to zinc, under these conditions, intense color reactions are given by copper (blue-violet color), cobalt (green), nickel (green). Cadmium, mercury, lead, etc. do not interfere with the detection of zinc.

Reagent VII has the following advantages over "zincon" [4].

1) The sensitivity of reagent VII is twice that of "zincon";

2) Zinc can be determined with reagent VII in the presence of considerably greater amount of cadmium.

Reagent XIX gives a selective reaction with palladium at a pH of about 5. The color change is from lilac to a dirty-blue. The sensitivity of the visual reaction is 0.25 μg palladium in 5 ml of solution. λ_{max} of the reagent is 540 mμ, while λ_{max} for the complex is 360 mμ; $\epsilon_{reagent}$ is $1.57 \cdot 10^4$ at 540 mμ, while $\epsilon_{complex}$ is $5.5 \cdot 10^3$ at 540 mμ.

The remaining elements of the platinum group do not lead to a change in the color of the reagent solution.

In addition to palladium, under these conditions, intense color reactions are also given by copper (blue), cobalt (blue), and nickel (violet).

Thus the results obtained confirm our assumption re the possibility of making reagents with an enhanced selectivity by including a weakly complexing azoxy group in the system of a polydentate chelate forming agent.

EXPERIMENTAL

Synthesis of Reagents. 2,2'-dihydroxyazobenzene (I), 2,2'-dihydroxyazobenzene (II), and 2,2'-diaminoazoxybenzene (V) were synthesized according to published methods [5, 6, 7]. The m. p. of I was 156°. The published figure [5] was m. p. 154-155°. The m. p. of II was 171-172°, while the published m. p. [6] was 172-172.7°. The m. p. of V was 115-116°, while the published m. p. [7] was 115°. Salicylidene-2-aminophenol(III) was presented by Lukin, its m.p. was 185.5-186.5° [8]. 2-amino-2'-hydroxy-5'-methylazoxybenzene (IV) was prepared according to [9]. The m. p. was 126°.

Found %: C 64.58, 64.29; H 5.62, 5.68; N 17.50, 17.36. $C_{13}H_{13}O_2N_3$. Calculated %: C 64.19; H 5.35; N 17.28.

General Observations on Synthesis

o', o"-Dihydroxy-o- azoazoxy compounds

The 2-amino-2'-hydroxy-5'-methylazoxybenzene in the filtrate obtained by the action of hydrazine on 2-phthaloylamino-2'-hydroxy-5'-methylazoxybenzene [9] was diazotized and coupled with the azo component. Diazotization was carried out with excess sodium nitrite. Excess nitrous acid was destroyed with urea. 1.4 g-mole of the azo component was used per g-mole 2-phthaloylamino-2'-hydroxy-5'-methylazoxybenzene. Coupling was carried out at 0-3°, the diazo solution was gradually added to the solution of the azo component. The dyes were isolated on the day following the coupling. The dyes were purified by reprecipitation or recrystallization from various solvents.

The theoretical yields indicated are given in all cases in terms of 2-phthaloylamino-2'-hydroxy-5'-methylazoxybenzene.

The methods used for purifying and isolating the dyes are given below.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-1")-2"-hydroxynaphthalene (VI) was synthesized according to [9].

2'-Hydroxy-5'-1'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-2")-1"-hydroxy-8"-aminonaphthalene-3",6"-disulfonic acid (VII) was dissolved in water and salted out with cooking salt. The yield was 23% of a dark-violet powder, readily soluble in water.

Found %: moisture content 7.6; NaCl 2.47; C 42.82, 42.79; N 10.44, 10.33; H 3.61, 3.54. $C_{23}H_{19}N_5O_9S_2$ assuming 7.6% moisture content 2.47 NaCl. Calculated %: C 43.3; H 3.81; N 10.9.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-1")-2"-hydroxynaphthalene-3",6"-disulfonic acid (VIII) was dissolved in NaOH and salted out with hydrochloric acid, it was washed with ice water and dried at 80-90°. Yield 20%.

Found %: C 50.17, 50.2; H 3.9, 4.0. $C_{23}H_{18}N_4O_9S_2$. Calculated %: C 49.64; H 3.23.

The powder which is dark-violet in color is readily soluble in water.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-1")-2", 4"-dihydroxybenzene (IX) was purified by acidifying the alcoholic alkali solution. Yield. 14.6%.

Found %: C 62.09, 62.03; H 4.63, 4.84. $C_{19}H_{16}N_4O_4$. Calculated %: C 62.63; H 4.39.

The powder is dark-brown in color. The material chars at 210°.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-2")-4", 5"-dimethylimidazole (X) was purified by successive recrystallization from ethanol and dioxane, and dried at 70°. Yield 10.5%.

Found %: C 61.66, 61.87; H 5.56, 5.58. $C_{18}H_{18}N_6O_2$. Calculated %: C 61.71; H 5.14.

The powder is orange in color; m. p. 200-202°.

(2'-Hydroxy-5'-methylbenzene-[1'-azoxy-1]-benzene-2)-phenylformazylbenzene (XI) was dissolved in alcoholic alkali, it was then salted out with hydrochloric acid, filtered off, washed with water and dried in a vacuum desiccator over calcium chloride and phosphorus pentoxide. Yield 10%.

Found %: C 68.58, 68.4; H 5.11, 5.30. $C_{26}H_{22}N_6O_2$. Calculated %: C 69.33; H 4.88.

The powder is dark-bordeaux in color; m. p. 138°.

1"-(2-)2"-Hydroxy -5'-methyl-benzene-(1'-azoxy-1)-phenyl-(3"-)-p-tolyl-(3"-hydroxytriazene) (XII) was recrystallized from a mixture of ethanol and chloroform (2:1) and dried in a vacuum desiccator over calcium chloride. Yield 11.7%.

Found %: C 63.45, 63.43; H 5.32, 5.36. $C_{20}H_{19}N_5O_3$. Calculated %: C 63.66; H 5.01.

The powder is orange in color; m. p. 145°.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-N)-α-benzaldoxime (XIII) was recrystallized from a mixture of ethanol and chloroform (2:1) and dried in a vacuum desiccator over calcium chloride. Yield 10%.

Found %: C 64.13, 63.87; H 5.17, 4.98. $C_{20}H_{17}N_5O_3$. Calculated %: C 54.0; H 4.53.

The powder is brown in color. It chars at about 200°.

2'-Hydroxy-5-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-7")-8"-hydroxyquinoline-5"-sulfonic acid (XIV) was purified by acidifying its alcoholic alkaline solution. The powder is reddish-brown in color.

Found %: N 11.07 (the nitrogen content of the azo- and azoxygroups was determined vanadometrically). $C_{22}H_{17}N_5O_6S$. Calculated %: N 11.6.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-1")-naphthalene 2"-iminodiacetic acid (XV) was purified by acidification of its alkaline solution. The powder is brown in color; m. p. 115-117°.

Found %: C 60.3, 60.6; H 5.07, 5.3. $C_{27}H_{23}N_5O_6 \cdot 1.5\,H_2O$. Calculated %: C 60.0; H 4.8.

1-Azoxyazomethine compound (XVI) obtained from 2-amino-2'-hydroxy-5'-methylazoxybenzene (IV) and salicaldehyde. To 0.002 g-mole of IV in ethanol was added 0.0025 g-mole of salicaldehyde, the mixture was heated for 30 minutes at 60-70°; the precipitate was then filtered off, washed with ethanol, recrystallized from 40 ml of a mixture of petroleum ether and chloroform (3:1), and dried in a vacuum desiccator over calcium chloride. The powder is yellow in color; m. p. 180°.

Found %: C 67.7, 67.95; H 5.51, 5.38; N 11.41, 11.37. $C_{20}H_{17}N_3O_3 \cdot 0.5\,H_2O$. Calculated %: C 67.4; H 5.06; N 11.8.

o,o'-Bisazoazoxy compounds obtained from 2,2'-diaminoazoxybenzene and 2-naphthol (XVII), p-cresol (XVIII), and H-acid (XIX). 2,2'-diaminohydroxybenzene was diazotized and coupled with 2-naphthol (2M), p-cresol (2M), and H-acid (2M). Coupling was carried out in a soda-alkaline medium. XVII was purified by successive reprecipitation of the acid from alcoholic alkali, and by petroleum ether from chloroform. The powder has a cherry red color; m. p. 238°.

Found %: C 71.55, 71.69; H 4.97, 5.0. $C_{32}H_{22}N_6O_3$. Calculated %: C 71.50; H 4.13.

Dye XVIII was dissolved in benzene and precipitated by petroleum ether. The powder is brown in color; m. p. 135°.

Found %: N 18.89, 18.60. $C_{26}H_{22}N_6O_3$. Calculated %: N 18.02.

Dye XIX was dissolved in water and salted out with cooking salt. The material was not obtained in a chemically pure state.

Test Methods

Method A (Extraction with nonaqueous solvents). Reagents (I-VI, IX-XIII, XV, XVI-XVIII) which are insoluble in water were tested in the form of their 0.001 M chloroform solutions. Into four microtubes were introduced successively 0.5 ml of the extractant, 0.15 ml of reagent solution, and 0.06 ml of 2 M NaOH, while, in addition, to the first three tubes was added 0.06 ml of the corresponding standard solutions of the inorganic salts (100 μg of the cation). To the fourth tube was added 0.06 ml of distilled water (control test); the tubes were then all shaken and any change in the color of the organic layer or the appearance of a precipitate noted. Shaking was carried out for about 1 minute. Subsequently, the solutions were titrated in succession with acid reagents (1 M CH_3COOH, glacial acetic acid, HNO_3 1:2, and H_2SO_4 1:3). Each color change in the organic layer was observed and a note was made at which pH values of the solutions this effect was observed. Chloroform was used as extractant. Carbon tetrachloride was used for extracting reagent VI. In parallel, experiments were carried out in which pyridine was also introduced (after addition of the reagent) at the rate of about 0.03 ml per 0.5 ml of organic solvent. During a study of the sensitivity of the reaction, the pH of the solutions was kept constant by means of buffer solutions.

Method B (Experiments in aqueous solutions). The reagents which are soluble in water VII, VIII, XIV, and XIX were tested in the form of their 0.01-0.001% aqueous solutions.

Into 12 test tubes were introduced 1 ml lots of reagent solution, this was followed by adding: to the first and second test tubes, 0.06 ml of a 10% solution of acetic acid and 0.45 ml of 15% sodium acetate solution (pH about 5.8); to the third and fourth test tubes, 0.03 ml of hydrochloric acid and 0.3 ml of a 20% solution of urotropine (pH about 6); to the fifth and sixth test tubes, 0.06 ml of a 10% solution of Na_2CO_3 (pH about 10); to the seventh and eighth, 0.06 ml of a 10% solution of NaOH (pH about 13); to the ninth and tenth test tubes, 0.09 ml of a 10% solution of ammonium chloride, 0.15 ml of 1% ammonia, and 0.18 ml of 25% solution of ammonia (pH about 9); to the eleventh, 0.09 ml of HNO_3 (1 : 3) (pH 1), after which to all the test tubes with an odd number was added 0.06 ml of the corresponding standard solutions of the inorganic salts (100 μg of the cation), while to all even numbered test tubes was added 0.06 ml of distilled water (control test). The test tubes were shaken and any changes in color of the solution noted. Shaking was carried out for 1 minute.

The Change in the Optical Density of the Solutions.* Concentration of reagent I, $4.35 \cdot 10^{-5}$ M, copper concentration $1.5 \cdot 10^{-5}$ g-atom/liter; concentration of reagent II, $4.7 \cdot 10^{-5}$ M, copper concentration $6.45 \cdot 10^{-6}$ g-atom/liter; concentration of reagent III, $4.8 \cdot 10^{-5}$ M, copper concentration $9 \cdot 10^{-6}$ g-atom/liter; concentration of reagent VI, $2.5 \cdot 10^{-5}$ M, concentration of reagent VII, $7 \cdot 10^{-5}$ M; zinc was taken in a 32-fold molar excess with respect to the reagent; concentration of reagent XIX, $1.1 \cdot 10^{-5}$ M; palladium was taken in a 32-fold molar excess with respect to the reagent. The pH of the solutions was kept constant by means of a buffer with a pH of 10 for reagents I-III, with a pH of 14 for reagent VI, and with a pH of 5 for reagent XIX. Reagents I, II, III, and VI which are insoluble in water were dissolved in chloroform (reagents I-III) or carbon tetrachloride (reagent VI), and mixed, in the case of reagents I-III, VII with a buffer which had a pH of 10.6, in the case of reagent VI with a buffer with a pH of 14, and in the case of XIX with a buffer with a pH of 5, and with an aqueous solution of the salt of the cation. The ratio of the aqueous and nonaqueous phases was 1 : 20 by volume. In the case of reagents I-III, 0.05 ml of pyridine was added for 20 ml of chloroform. The mixture was shaken for 5-10 minutes; the nonaqueous layer was filtered off and the optical density measured on a SF-4 spectrophotometer, the thickness of the layer in the cuvette being 1.0 cm; the optical density was measured relative to chloroform for reagents I-III, to carbon tetrachloride for reagent VI, and to water for reagents VII and XIX.

The optical density of complexes for reagents I-III was calculated on the basis of the cation concentration, and for reagents VII and XIX on the basis of the molar concentration of the reagent. The optical density for all the reagents was calculated with respect to the amount of reagent added initially.

SUMMARY

The enhanced selectivity of 2,2'-dihydroxyazoxybenzene as compared with that of the analogous azo- and azomethine compounds has been established in reactions with cations.

The inclusion of an azoxy group in the system of a polydentate chelate forming agent leads to the formation of sensitive reagents with enhanced selectivity.

Among o',o"-dihydroxyazoxyazo compounds and o,o'-bis-(o-hydroxyazo)-azoxy compounds, reagents have been found which are of interest for the photometric determination of calcium, zinc, and palladium.

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THE REDUCING PROPERTIES OF ETHYLENEDIAMINETETRACETIC ACID

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Published data of a qualitative character [1-5] testify to the fact that under certain conditions, Ce^{IV}, Mn^{VII}, V^{V}, $S_2O_8^{2-}$, etc. oxidize ethylenediaminetetracetic acid (EDTA). Establishment of the quantitative relationships which hold during the oxidation of EDTA is of definite interest for solving a number of analytical problems. Our work was therefore directed at a detailed study of the reducing properties of EDTA and its salts.

The following materials were used: 1) sodium ethylenediaminetetracetate (EDTA – Na) (molecular wt. 372.2) which was purified by precipitation with methanol from an aqueous solution [6], and EDTA which was obtained from its sodium salt [7].

2) Solutions of the oxidizing agents: 0.043 M solution of ceric sulfate; 0.080 M ammonium vanadate; and 0.100 M potassium permanganate.

3) 0.027 M and 0.05 M solutions of EDTA – Na.

Experiments showed that the permanganate ion in a 1-2 N solution of sulfuric acid can be quantitatively titrated with EDTA-Na solution (and vice versa) in the cold. The titration end point was established visually from the disappearance of the permanganate color. The titration results are given in Table 1.

TABLE 1

Titration of 0.100 N $KMnO_4$ Solution with 0.027 M EDTA-Na

Amount of $KMnO_4$, g-eq $\times 10^{-3}$	Amt. of EDTA-Na used, g-mole $\times 10^{-3}$	Ratio of EDTA-Na (g-mole) to Mn^{VII} (g-eq.)
0.100	0.0124	1 : 8.05
0.100	0.0127	1 : 7.87
0.100	0.0124	1 : 8.05
0.200	0.0248	1 : 8.05

Complete decolorization is observed at a ratio of one mole of EDTA-Na to eight gram equivalents of the oxidizing agent.

Results for the titration of 0.043 M ceric sulfate solution with 0.050 M EDTA-Na at a pH of 1-1.5 in the cold, and on warming, are given in Table 2 (the titration end point was again determined visually by the disappearance of the color of quadrivalent cerium). Quadrivalent cerium in an acid medium (pH 1-1.5) reacts with EDTA-Na in the cold in the proportion of 1 : 4, while on heating, it reacts in the proportion of 1 : 8.

Quinquevalent vanadium and sexivalent chromium, as experiments showed, are reduced in an acid medium (1 N H_2SO_4) only on heating, and in the presence of excess EDTA-Na.

TABLE 2

Titration of $Ce(SO_4)_2$ with EDTA-Na (0.215 g-eq of Ce^{IV} taken)

Experimental conditions	EDTA-Na used, g-mole $\times 10^{-3}$	Ratio of EDTA-Na (g-mole) to Ce^{IV} (g-eq.)
In the cold	0.0540	1 : 4.0
In the cold	0.0545	1 : 3.95
On heating	0.0270	1 : 8.0
On heating	0.0265	1 : 8.1

During the oxidation of EDTA by septivalent manganese, quinquevalent vanadium, etc., carbon dioxide is liberated. Results on the quantitative determination of the carbon dioxide formed during the oxidation of EDTA-Na (by absorbing the CO_2 with askarite) are given in Table 3. With increasing ratio of oxidizing agent (Ce^{IV} or Mn^{VII}) to EDTA, the number of moles of carbon dioxide liberated per mole of EDTA-Na increases (figure).

TABLE 3

Amount of CO_2 Formed During the Oxidation of EDTA by Solutions of Ce^{IV}, Mn^{VII}, and V^V (on heating in a medium of 1 N H_2SO_4)

Oxidizing agent	Amt. of oxidizing agent, g-eq. $\times 10^{-3}$	EDTA-Na added, g-mole $\times 10^{-3}$	Ratio of EDTA-Na (g-mole) to oxidizing agent (g-eq)	CO_2 liberated, g-mole $\times 10^{-3}$	Ratio of CO_2 (g-mole) to oxidizing agent (g-eq)	Ratio of CO_2 (g-mole) to EDTA-Na (g-mole)
Ce^{IV}	0.210	0.430	2 : 1	0.100	1 : 2	0.23 : 1
	0.210	0.210	1 : 1	0.097	1 : 2	0.46 : 1
	0.420	0.460*	1 : 1	0.200	1 : 2	0.43 : 1
	0.210	0.105	1 : 2	0.100	1 : 2	1 : 1
	0.210	0.053	1 : 4	0.095	1 : 2	1.8 : 1
	0.210	0.042	1 : 5	0.100	1 : 2	2.4 : 1
	0.210	0.035	1 : 6	0.097	1 : 2	2.8 : 1
	0.210	0.027	1 : 8	0.100	1 : 2	3.7 : 1
	0.420	0.053	1 : 8	0.200	1 : 2	3.8 : 1
	0.210	0.021	1 : 10	0.084	1 : 2.5	4 : 1
	0.210	0.014	1 : 15	0.048	1 : 4.4	3.4 : 1
V^V	0.400	1.60	4:1	0.200	1 : 2	—
	0.800	2.00	2.5 : 1	0.400	1 : 2	—
	0.800	2.00*	2.5 : 1	0.400	1 : 2	—
	0.400	0.80	2 : 1	0.200	1 : 2	—
	0.600	1.60	2 : 1	0.400	1 : 2	—
	0.800	0.80	1 : 1	0.300	1 : 2.7	—
	0.800	0.40	1 : 2	0.130	1 : 6	
Mn^{VII}	0.100	0.020	1 : 5	0.046	1 : 2.1	2.3 : 1
	0.100	0.012*	1 : 8.3	0.046	1 : 2.1	3.8 : 1
	0.100	0.012	1 : 8.3	0.048	1 : 2.0	4 : 1
	0.200	0.024	1 : 8.3	0.095	1 : 2.1	4 : 1
	0.100	0.010	1 : 10	0.043	1 : 2.3	4.3 : 1

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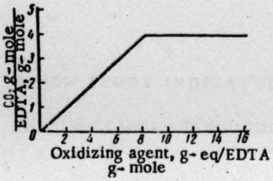
* An accurately weighed aliquot of EDTA was taken.

During the oxidation of EDTA there is observed on the curves (figure) a break at a ratio of oxidizing agent g-eq. to EDTA equal to 8 :1, corresponding to the liberation of four moles of carbon dioxide to one mole of EDTA; on increasing the amount of oxidizing agent further, this ratio remains constant and equal to four. Accordingly, in an acid medium, the molecule of ethylenediaminetetracetic acid, under the influence of the oxidizing agent, breaks down to yield four molecules of carbon dioxide; during this process, it is obviously the carboxyl groups which break down.



Liberation of CO_2 during oxidation of EDTA by $Ce(SO_4)_2$ and $KMnO_4$ solutions.

EDTA is used in several analytical methods in combination with hydrogen peroxide, but the possibility of the oxidation of the EDTA has not been taken into account. According to our observations, EDTA is oxidized by excess 30% hydrogen peroxide in both acid and alkaline media. On heating to the boil this reaction proceeds quantitatively in a few minutes; in the cold only about 20% of the EDTA is oxidized in 18-20 hours (this was established by titrating the residual EDTA with a magnesium salt solution). We were unable to isolate and identify any other oxidation products of EDTA, apart from CO_2. It should be pointed out that Czech workers [8] during a polarographic study of the products obtained during the oxidation of EDTA by lead peroxide, demonstrated that formaldehyde is formed. In addition, these authors suggest the formation of products formed by the condensation of formaldehyde with amines, which are also obtained during the oxidation of EDTA.

SUMMARY

It has been found that ethylenediaminetetracetic acid (EDTA) interacts with septivalent manganese (in 1-2 N H_2SO_4) in the proportion of one mole of EDTA to eight gram equivalents of the oxidizing agent; in the case of quadrivalent cerium the relationship indicated is only observed on heating.

Quinquevalent vanadium and sexivalent chromium are reduced in an acid medium, only on heating and in the presence of excess EDTA.

Excess hydrogen peroxide, in both acid and alkali media, oxidizes EDTA; the reaction is quantitative and rapid only when the solution is boiled.

In acid media the EDTA molecule breaks down under the influence of oxidizing agents to liberate four molecules of carbon dioxide.

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* Original Russian pagination. See C. B. translation.

A NEW REDOX INDICATOR FOR TITRATION IN ALKALINE MEDIA

THE FERRICYANIDE METHOD FOR THE DETERMINATION OF VANADIUM

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Oxidimetry in alkaline media has been developed to a comparatively small extent. It is only in recent years that papers have started to appear which are devoted to the determination of oxidizing or reducing agents in alkaline media [1-9]. In most cases, the methods described in these papers have a potentiometric finish. Various diphenylamine derivatives [10] have been tested as redox indicators under the conditions indicated; diphenylaminosulfonic acid in the oxidized form has proved to be best indicator. When it is borne in mind that this compound only has a low sensitivity, that its oxidation products exhibit maximum absorption on the short wave side of the visible spectrum, and that is not very easy to prepare the "polyoxidized" form of this indicator, it is quite obvious that it is necessary to make a further search for indicators which are suitable for oxidation – reduction titrations in alkaline media.

It was shown recently in our laboratories that certain diphenylbenzidene derivatives possess high sensitivity toward oxidizing agents at high pH values [11], although their oxidation products too exhibit maximum light absorption in the short-wave region of the spectrum. But, e.g., diphenyldianisidine-o,o'-dicarboxylic acid, which we shall henceforth refer to as "redoxal", and which we were the first to synthesize, possesses a high sensitivity to oxidizing agents in alkaline media and has a soluble oxidized form bright-red in color (Fig. 1). The indicator exhibits the maximum sensitivity for the ferricyanide ion in an alkaline medium, as compared with the other materials studied (Table 1).

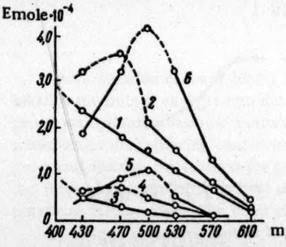


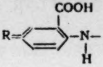
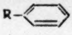
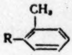
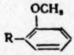
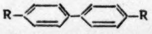
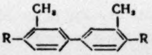
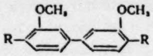
Fig. 1. Light absorption curves for $0.68 \cdot 10^{-4}$ M solutions of the reagents (oxidizing agent – potassium ferricyanide). 1) Diphenylbenzidene-o,o'-dicarboxylic acid; 2) diphenyltolidene-o,o'-dicarboxylic acid; 3) phenylanthranilic acid; 4) o-tolylanthranilic acid; 5) o-anisidene-anthranilic acid; 6) diphenyldianisidine-o,o'-dicarboxylic acid.

The oxidation-reduction potential of redoxal in 1 M potassium hydroxide proved to be equal to 0.304 v with respect to the normal hydrogen electrode. The oxidized form of the indicator, as indicated already, is bright red in color, while the reduced form is colorless; the color change is reversible.

During the interaction of the reagent studied with potassium ferricyanide in an alkaline medium, the color appears instantaneously and reaches a maximum in 2.5 minutes. This latter fact does not impose any limitations on the use of the indicator, this is demonstrated by the curve shown in Fig. 2 which characterizes the change in optical density of a solution of the indicator with time. In the same diagram are also given curves which show that excess oxidizing agent has hardly any effect on the color intensity of the oxidized form of the indicator.

TABLE 1

Sensitivity of Some Diphenylamine and Diphenylbenzidene Derivatives to the Ferricyanide Ion In An Alkaline Medium (Determined by a Spot Test)

Reagent	Formula 	Color of the reaction product	Lim. of ident. µg	Limiting dilution
1. Phenylanthranilic acid		Brown-yellow	230	1 : 4300
2. o-Tolylanthranilic acid		Red-brown	23	1 : 43 000
3. o-Methoxyphenyl-anthranilic acid		Red	23	1 : 43 000
4. Diphenylbenzidene-o,o'-dicarboxylic acid		Brown-yellow	2.3	1 : 430 000
5. Diphenyltolidene-o,o'-dicarboxylic acid		Red-brown	0.5	1 : 2 000 000
6. Diphenyldianisidine-o,o'-dicarboxylic acid		Red	0.4	1 : 2 500 000

The color formed is stable on diluting the solution (Table 2). Figure 3 shows that changes in alkalinity over a wide range do not affect the rate at which the maximum color develops.

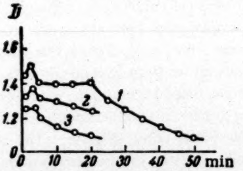


Fig. 2. Stability of the color of redoxal in the oxidized form with time. 1) 0.33 ml of 10^{-3} M solution of redoxal, 0.66 ml of 10^{-3} M potassium ferricyanide, and 4 ml of 0.1 N sodium hydroxide; 2) ditto, but with 1.32 ml of ferricyanide; 3) ditto but with 2.00 ml of ferricyanide.

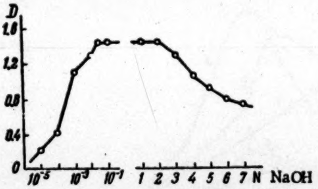


Fig. 3. Effect of sodium hydroxide concentration on the color intensity of the oxidized form of redoxal (0.3 ml of 10^{-3} M redoxal solution, 0.66 ml 10^{-3}M potassium ferricyanide, and 4 ml of sodium hydroxide solution of varying concentration).

We have studied the possibility of using redoxal as a redox indicator for the titration of ferricyanide with quadrivalent vanadium salts. 0.05 N solutions of vanadyl tartrate and vanadyl sulfate were used as reducing agents; vanadyl sulfate was prepared according to the method of Willard and Manalo [10]. The concentration of the vanadyl sulfate solution was determined by means of permanganate [13], while that of the ferricyanide was determined iodometrically [12].

The indicator was prepared by dissolving 0.0240 g of diphenyldianisidine-o,o'-dicarboxylic acid and 0.0240 g of sodium carbonate in 50 ml of water.

TABLE 2

The Stability of the Color of Oxidized Redoxal on Diluting with 0.1 N Alkali ($C_{\text{initial}} = 5\cdot10^{-5}$ M; l = 0.5 cm)

Solution	Optical density
Original	1.41
Diluted 1 : 1	0.70
Diluted 1 : 4	0.35
Diluted 1 : 8	0.18

Titration was carried out as follows: to 5 ml of $5\cdot10^{-2}$ or $5\cdot10^{-3}$ N potassium ferricyanide solution was added 20 ml of water and the corresponding amount of 10 N NaOH; Saratov natural gas* was passed through the solution for 10 minutes to remove dissolved oxygen; after addition of three drops of the indicator solution and one drop of cupric sulfate,** titration was carried out with an equimolar solution of vanadyl sulfate or vanadyl tartrate, until the red color of the solution being titrated changed instantaneously to a yellow-green color or the solution became colorless.

The experimental results obtained are summarized in Table 3.

TABLE 3

Effect of Alkalinity and Dilution on the Accuracy of Titrating Potassium Ferricyanide Solution with Solutions of Vanadyl Sulfate and Vanadyl Tartrate, Using Redoxal as Indicator

Conc. of titrated sol., g-mole/liter		$5\cdot10^{-2}$					$5\cdot10^{-3}$	
Expt. No.		1	2	3	4	6	1	2
Amount of 10 N NaOH added to the solution being titrated, ml		0.5	1.0	2.0	5.0	10.0	2.5	5.0
Solution used, ml	Vanadyl sulfate	5.10	5.00	5.00	5.00	4.96	4.98	4.96
	Vanadyl tartrate	4.90	5.00	5.00	5.00	4.96	4.98	4.96

Back titration of the reducing agent with vanadyl sulfate as oxidizing agent is impossible, since, in an alkaline medium, it changes into the hydroxide. Vanadyl tartrate under these conditions, although it does not give a precipitate, gives low results during titration, as is evident from Table 4, in which are given results obtained under the following conditions: to 20 ml of water was added a definite amount of 10 N NaOH and natural gas passed through the solution for 10 minutes, 5 ml of $5\cdot10^{-2}$ N vanadyl tartrate was then added, followed by 2-3 drops of indicator solution and one drop of cupric sulfate; the solution was finally titrated with $5\cdot10^{-2}$ N potassium ferricyanide. The color change is sharp, from green to red.

Quadrivalent vanadium and tartaric acid in an acid medium forms [14] a complex $[VO(HC_4H_4O_6)]^+$, while at pH 6 the complex $[VO(C_4H_4O_6)_2]^{2-}$ is formed; the latter is stable in alkaline media. In this connection, we have made an attempt to determine vanadium in the form of vanadyl tartrate by adding sodium potassium tartrate to a solution of ammonium vanadate*** on heating, and rapidly titrating the hot solution with potassium ferricyanide after making the solution alkaline.

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* Replacement of the natural gas by nitrogen has no effect on the experimental accuracy; oxidation of sulfur compounds, which may be present in the gas, by the potassium ferricyanide, occurs, as is well-known, under fairly rigorous conditions [9].

** Cupric ions increase the rate at which the ferricyanide reacts with quadrivalent vanadium salts.

*** Tartaric and citric acids, and their salts, convert VO_3^- to VO^{2+} [15].

We found that determination of vanadium can indeed be carried out in this way, it is even possible to titrate 10^{-3} N solutions; there is no need to pass an inert gas through the solution in this case (Table 5).

TABLE 4

The Possibility of Titrating Vanadyl Tartrate with $5 \cdot 10^{-2}$ N Potassium Ferricyanide Solution in the Presence of Redoxal

Expt. No.	1	2	3	4
Amt. of 10 *N* NaOH, added, ml	0.5	1.0	2.0	5.0
Amount of $5 \cdot 10^{-2}$ *N* ferricyanide solution used, ml	4.78	4.90	4.90	4.90

Six times its amount of chromium, twice its amount of manganese, twice its amount of molybdenum, and 12 times its amount of tungsten do not interfere with the determination of vanadium. Nickel and trivalent iron can be present in large amounts; cobalt and divalent iron (as its complex with tartaric acid) are titrated in the same way with potassium ferricyanide under the experimental conditions used.

The method suggested for the determination of vanadium is applicable to the analysis of iron based alloys (steel, ferrovanadium). The method is particularly suitable for the analysis of high silicon rocks, containing vanadium, since, by using this method, it is possible to avoid the lengthy process of removing silicic acid.

TABLE 5

Effect of Alkalinity on the Accuracy of Titration with Potassium Ferricyanide of Vanadyl Tartrate Obtained by Reduction of Ammonium Vanadate with Tartaric Acid (11.40 mg V taken)

NaOH concentration, N	V found, mg
1.2	11.11
2.2	11.37
3.0	11.37
3.6	11.37
4.2	11.37
4.5	11.37

TABLE 6

Determination of Vanadium in Rocks

Sample No.	Vanadium found, %	
	colorimetrically as a heteropolyacid [16]	by the suggested method
1	0.73	0.76
2	0.47	0.48
3	1.75	1.80
4	1.19	1.22

Vanadium is determined in rocks as follows: one g of finely ground sample is fused with a mixture of 4 g of sodium carbonate and 2 g of potassium carbonate. The melt is leached with hot water. The precipitate of sesquioxides is filtered off. The filtrate is placed in a 100 ml standard flask. An aliquot of the solution (10-20 ml) is acidified with sulfuric acid (using congo red paper), 10 ml of a saturated solution of sodium potassium tartrate is added and the whole heated to the boiling point, and then boiled for 1-2 minutes. The yellow color of the test solution, which is determined by the presence of the compound of quinquevalent vanadium with tartrate, disappears, and the solution acquires a blue color when large amounts of vanadium are present. To the hot solution is added 10 ml of 40% sodium hydroxide, three drops of indicator solution, one drop of a 1% cupric sulfate solution and the final solution titrated with .01N potassium ferricyanide until a red color appears. The potassium ferricyanide solution is standardized against ammonium vanadate under identical conditions.

The method was tried out on four samples of rock (Table 6).

For the analysis of steel, 0.3000 g is dissolved in 20 ml of hydrochloric acid 1:1. When the sample has dissolved completely the solution is heated to the boil, 5 ml of concentrated nitric acid is added, and the solution boiled to remove nitrogen oxides. The tungstic acid precipitate formed is filtered off and the filtrate collected in a 100 ml standard flask. The sesquioxides are precipitated in the standard flask with 40% sodium hydroxide, a small excess of the latter being taken (1-2 ml). The contents of the flask are made up to volume with water, the whole carefully mixed, and then filtered into a dry flask. 10-20 ml of the filtrate is taken for titration, and the procedure given for the analysis of rocks then followed. When the vanadium content of the steel is less than 1%, 50 ml of the filtrate is taken for titration. For the analysis of ferrovanadium the amount of sample taken is reduced to 0.1000 g.

The method gives good results for steels with a high tungsten content; steels which contain molybdenum cannot, however, be analyzed by this method.

An idea of the accuracy of the method can be gained from the results given in Table 7.

TABLE 7

Determination of Vanadium in Iron Based Alloys

Sample	Specified vanadium content, %	Vanadium found, %
Ferrovanadium, Standard Sample 77	38.42	38.88; 38.79; 38.46
Steel, Standard Sample 87	2.26	2.20; 2.22
" " " 26 b	1.17	1.24; 1.22
" " " 122	1.85	1.81; 1.80
Steel, vanadium-nickel	0.26	0.24; 0.26
Steel, chrome-vanadium-tungsten	2.23	2.38; 2.30

Synthesis of Diphenyldianisidine-o,o'-dicarboxylic Acid. Twenty ml of isoamyl alcohol, 2.5 g of o-chlorobenzoic acid, 2 g of o-dianisidine, 2.7 g of potassium carbonate, and 0.1 g of powdered copper metal are boiled for two hours under reflux. The isoamyl alcohol is removed by steam distillation, and the acid precipitated from the solution of its potassium salt with hydrochloric acid solution 1:1. The material is purified by reprecipitation, and then by dissolving in ethanol on heating, and precipitating with water. The diphenyldianisidine-o,o'-dicarboxylic acid purified in this way is a light-green powder with an indefinite m. p. of about 300°. The molecular weight as determined by Rast's method (in benzoic acid) proved to be 485.2. The theoretical value is 484. The following values were obtained during nitrogen determinations:

$C_{28}H_{24}O_6N_2$. Calculated %: N 5.66, 5.75; Found %: N 5.78.

SUMMARY

Diphenyldianisidine-o,o'-dicarboxylic acid has been synthesized for the first time. In connection with the possibility of using it as a highly sensitive redox indicator in alkaline media it has been called "redoxal". The indicator gives a color change which is instantaneous and contrasting. It has been used for the direct and back titration of quadrivalent vanadium salts with potassium ferricyanide in an alkaline medium. The method described for the determination of vanadium is applicable to the analysis of rocks and iron based alloys.

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* Original Russian pagination. See C. B. translation.

TITRATION OF WEAK BASES IN ACETIC ACID AND IN ITS MIXTURES WITH ACETIC ANHYDRIDE BY MEANS OF AN ANTIMONY ELECTRODE

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Mixtures of acetic acid and acetic anhydride have long been used where acid solvents are required in analytical chemistry practice. It has been shown that addition of acetic anhydride to acetic acid enables tertiary amines to be determined separately in the presence of primary and secondary amines [1, 2]. Russell and Cameron [3] are of the opinion that excess of acetic anhydride in acetic acid significantly increases the acidity of sulfuric acid solutions. Tomiček and Heyrovsky [4] have established a relation between additions of anhydride and the potential of the hydrogen electrode in solutions of perchloric acid and sodium acetate. It has been shown [5] that even small additions of acetic anhydride to acetic acid change the acidity of the solutions appreciably, and improve the conditions of acid-base titration. When acetic anhydride is present, it is not only the acidity of sulfuric acid solutions which is increased [3], but also that of perchloric acid [6]. Thus, the increase in acidity is observed for all acids, and is not related – as suggested by Russell and Cameron – to the formation of a mixed anhydride possessing super acid properties.

The increase in acidity of solutions when acetic anhydride is present can be used for improving acid-base titration conditions not only in acetic acid [6-9], but also in other solvents, e.g., in nitromethane [7].

What is still uncertain is the optimum amount of acetic anhydride for acid-base titration in acetic acid. Russell and Cameron, Tomicek and Heyrovsky, and also the authors of [6], have studied the relation between the size of the potential jump and the acetic anhydride content up to 30-40%; it was shown that a significant increase in the potential jump is only observed on addition of the first portions of acetic anhydride, further increases in the amount of acetic anhydride (up to 40%) do not essentially affect the potential jump. Fritz and Fulda [7] found that during titration of a base in nitromethane containing 5, 20, and 50% of acetic anhydride, similar curves were obtained, i.e., addition of more than 5% acetic anhydride does not improve titration conditions.

In this connection we have studied the change in the potential jump of the indicator electrode for solutions of acids and bases, as a function of the solvent composition: from 100% acetic acid to 100% acetic anhydride. Many research workers have indicated that very weak bases whose pK values in water are greater than 12, are not titrated in acetic acid [6, 11-14]. However, on the basis of data on the dissociation constants of bases in acetic acid, and the known Roller ratio [15] $cK_B > 27 K_i$, it can be concluded that bases which are very weak in water (pK > 12) should be titrated in anhydrous acetic acid, and not only in mixtures of the latter with acetic anhydride. Since excess anhydride in acetic acid essentially changes the acidity of solutions of acids and bases, one might expect an improvement in the titration conditions of very weak bases (urea, caffeine, etc.) in mixtures of acetic acid and acetic anhydride. The possibility of such titration was studied in the work described here.*

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* When the work described here had been finished in 1955, articles [8, 9] were published which described the use of a mixture of acetic acid and acetic anhydride for the titration of very weak bases.

It is known from the practice of acid-base titration in nonaqueous media [18], that the glass electrode does not always give good results. This is also true of acid solvents, particularly for mixtures of acetic acid and acetic anhydride. Accordingly, we set ourselves the aim of studying the possibility of using an antimony electrode for acid-base titration in mixtures of acetic acid and acetic anhydride.

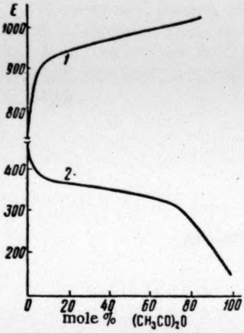

Fig. 1. Change in the emf of the quinhydrone-calomel electrode as a function of the solvent composition: 1) in 0.01 M perchloric acid solution; 2) in 0.01 M pyridine solution.

Experimental Part. Anhydrous acetic acid was prepared from glacial acetic acid by freezing the latter several times, and then distilling it under conditions excluding access to moisture; the final product had a m. p. of 16.6°. Acetic anhydride was prepared by fractionation of the commercial product, the fraction with a boiling point of 139.6° being collected.

The following chemically pure bases were used: pyridine, caffeine, urea, theobromine, and thiourea. Titration was carried out with 0.1 N perchloric acid. Solutions of the bases (0.01 M) and perchloric acid for titration were prepared in anhydrous acetic acid containing 20% acetic anhydride, and in 100% acetic anhydride. During the study of the effect of the composition on the potential jump, 0.01 M solutions of perchloric acid, sodium acetate, and pyridine were used. In the latter case the following circuits were used: quinhydrone – calomel electrodes, and antimony – silver chloride electrodes. Titration was carried out by means of a circuit of antimony – silver chloride electrodes, the silver chloride being immersed in a saturated solution of potassium chloride in 20% acetic anhydride. The antimony electrode used for titration in acetic acid was used earlier by Tomicek and Heyrovsky [4]. Its potential was established rapidly, the titration curves for strong bases (pyridine, sodium acetate) are more symmetrical than those obtained with other electrodes.

All measurements and titrations were carried out at room temperature.

In Fig. 1 is shown the change in emf of the quinhydrone – calomel circuit in 0.01 M perchloric acid and pyridine solutions as a function of the solvent composition. In Figs. 2, 3, 4, and 5 are shown titration curves of bases which are weak in water (pK > 13) in anhydrous acetic acid, and in mixtures of the latter with acetic anhydride and water. When thiourea is titrated in the presence of acetic anhydride two breaks are observed on the titration curve. Experiments showed that separate titration of bases is possible in mixtures of acetic acid and acetic anhydride, or in pure acetic anhydride. During titration the following circuit was set up:

$$\mathrm{Sb}\left|\begin{array}{l}\text{Base}\\ \text{solution}\end{array}\right|\begin{array}{l}\mathrm{KCl,\ AgCl/Ag}\\ \mathrm{CH_3COOH + 20\%\ (CH_3CO)_2O}\end{array}$$

The dissociation constants of the bases were calculated from the titration curves by means of Roller's equation [16], as we did earlier in other papers [5, 17]. The pK values obtained are given in the table.

pK of Weak Bases in Water, Acetic Acid, and Acetic Anhydride

Base	pK in water	pK in acetic acid		pK in acetic anhydride (by titration curves)
		by electroconductivity	by titration curves	
Pyridine	8.85	4.45	4.4	3.7
Caffeine	13.39	—	7.05	—
Urea	13.82	8.3	7.3	5.5
Theobromine	13.89	—	6.2	—
Thiourea	14.96	—	6.89	6.7

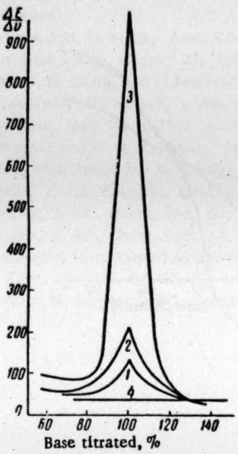

Fig. 2. Curves obtained during titration of 0.01 M urea solution with 0.1 M perchloric acid in mixtures of acetic acid with acetic anhydride and water: 1) in 100% acetic acid; 2) in a mixture of 80% acetic acid and 20% acetic anhydride; 3) in pure anhydride; 4) in acetic acid to which 1% water has been added.

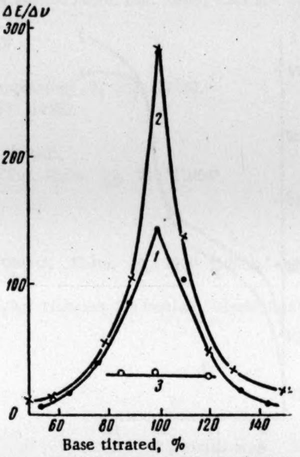

Fig. 3. Curves obtained during titration of 0.01 M caffeine solution with 0.1 M perchloric acid: 1) in 100% acetic acid; 2) acetic acid containing 20% acetic anhydride; 3) in acetic acid containing 0.5% water.

Discussion of Results. An examination of the curves relating potential to solvent composition shows that an essential change in potential occurs on adding the first portions of acetic anhydride to the acetic acid and on the addition of small amounts of acetic acid to acetic anhydride (Fig. 1). On the basis of these curves it can be concluded that for acid – base titration, the best solvent to use is acetic acid to which has been added 10-20%, or, even better, 85-95% acetic anhydride. The most favorable conditions for titration, with respect to the magnitude of the potential jump, are obtained when acetic anhydride is used as solvent.

Even bases which are very weak in water, with a pK in water of 13-15 (urea, caffeine, theobromine, thiourea, etc.) are titrated in anhydrous acetic acid. Consequently, the opposite view of some research workers [11-14] does not seem justified. Apparently, the solvent used by these workers must have contained small amounts of water. As our results have shown, when 1-0.5% of water is added to acetic acid (Fig. 2, Curve 4; Fig. 3, Curve 3) the break on the titration curve disappears. On the other hand, on addition of acetic anhydride to acetic acid, the titration sensitivity increases, and the potential jump returns. The best conditions are obtained in acetic anhydride (90-100%). Some bases, however, e.g., caffeine and theobromine, do not dissolve in acetic anhydride. Accordingly, it is better to use mixtures containing about 20% of the anhydride for these bases, while it is better to use 0.1 M instead of 0.01 M solutions of the bases themselves.

The improvement in the titration conditions on adding acetic anhydride to acetic acid can be explained by a decrease in the ionic product of the medium, and by an increase in the dielectric permeability of the solvent.

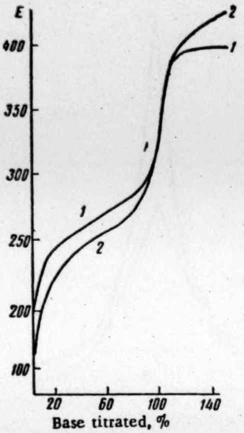

Fig. 4. Curves obtained during titration of 0.01 M theobromine solution with 0.1 M perchloric acid. 1) In 100% acetic acid; 2) in acetic acid containing 20% acetic anhydride.

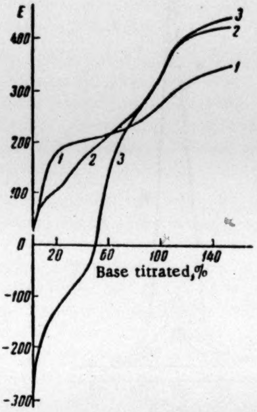

Fig. 5. Titration of 0.01 M thiourea solution with 0.1 M perchloric acid: 1) in 100% acetic acid; 2) in acetic acid containing 20% acetic anhydride; 3) in 100% acetic anhydride.

SUMMARY

The effect of additions of acetic anhydride to acetic acid [from 100% CH_3COOH to 100% $(CH_3CO)_2O$] on the value of the potential jump in solutions of acids and bases has been studied. The curves relating potential and solvent composition make it possible to choose the most favorable solvent composition (a mixture of acetic acid and acetic anhydride) for acid— base titration.

It has been shown that very weak bases – urea, caffeine, theobromine, and thiourea (in water $pK > 12$) – are titrated in anhydrous acetic acid; when even only small amounts of water are present, the bases indicated are not titrated in acetic acid; addition of acetic anhydride to acetic acid significantly improves the titration conditions of bases. The largest potential jump is observed when pure acetic anhydride is used.

The dissociation constants of pyridine, urea, caffeine, theobromine, and thiourea in anhydrous acetic acid and in acetic anhydride have been determined by means of the titration curves.

It has been shown that an antimony electrode is fully applicable for acid – base titration in acetic acid, and in mixtures of the latter with acetic anhydride.

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THE PROPERTIES OF ION EXCHANGE MEMBRANES

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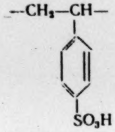
A study of the properties of ion exchange membranes opens up further possible applications of these materials. Electroion exchange setups, provided with ion exchange membranes, are used for desalting or concentrating solutions, and for the separation of cations from anions [1-5]. Electroion exchange methods of separating mixtures of ions, based on differences in the diffusion rate of ions of different valences and dimensions in ion exchange membranes under the influence of a constant electric field, are acquiring more and more interest. In this way, it is possible to separate ions which have such similar properties as magnesium and calcium ions [6], ions of isotopes, sodium and potassium ions, and to produce water enriched with D_2O [7], and to separate organic acids [8]. Ion exchange membranes are also used as electrodes which have a number of advantages of glass electrodes [9]; it is possible by means of ion exchange membranes to extract ions from solutions which are difficult to filter [10]. Ion exchange membranes can be used for the simultaneous extraction of cations and anions from solution.

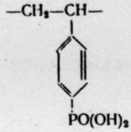
The diverse uses to which ion exchange membranes are put necessitates an all-around study primarily of the relation between the electrical properties and the structure of the ion exchange resin, the type of ionogenic groups involved, and the ion exchange properties. Such systematic studies have been carried out by Belinskaya and Materova [11]. Analysis of the results have shown that the electrode behavior of the membranes is determined by the type of ionogenic groups in the ion-exchange resin chosen, while the transport number is determined by the concentration of the ionogenic groups in the membrane. Titov [12] has carried out a study on the relation between the properties of the membrane and the capacity, and the degree of swelling of cation-exchange resins. He established that the resistance of sulfonate cation-exchange resins drops with increasing capacity of the cation-exchange resin and its degree of swelling; the transport number and the mechanical stability of the membranes do not depend on the capacity of the cation exchange resin, and drop with increasing degree of swelling. All the studies indicated were carried out on ion-exchange resins whose macromolecules had different structures.

In developing these studies, we have made a comparison of the ion-exchange properties of ion-exchange resins and of the electrical resistance of membranes prepared from these resins. A method of preparing heterogeneous membranes was chosen [9, 13]. Membranes with maximum mechanical stability, chemical stability, and thermal stability can be prepared by using rubber as a binder, particularly chloroprene rubber or carboxylate copolymers of styrene and divinyl. The ion-exchange membranes were prepared under identical conditions. The amount of ion-exchange resin in the membrane was 70%. The ion-exchange resins were ground beforehand in a jet mill until the particle size was 10-40 μ. In order to compare the effect of the type of ionogenic group on the ion-exchange properties of the ion-exchange resin and on the electrical conductivity of the membranes, we considered it necessary to choose ion-exchange resins the structure of whose macromolecules was the same. On this basis, we chose a copolymer of styrene and divinylbenzene which is characterized by the fact that the macromolecules have a distinct structure, and the highest stability in subsequent chemical transformations.

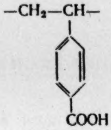
The copolymer chosen had a swelling coefficient of 2.0 in benzene. Methods and conditions for introducing acid and basic groups into the resin were developed specifically for this copolymer. As a result, we obtained a selection of ion-exchange resins in which the macromolecules had the same structure, while they contained different ionogenic groups:



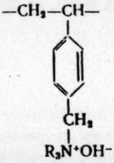
Cation exchange resin SDV



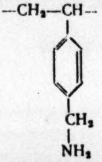
Cation exchange resin SF



Cation exchange resin KS



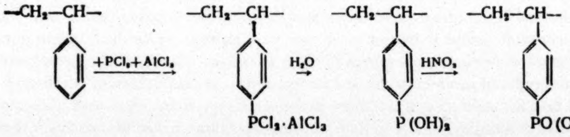
Anion exchange resin ASD-v



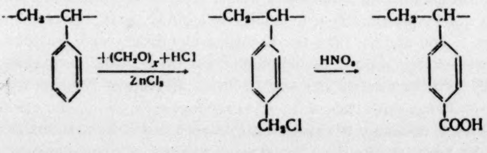
Anion exchange resin ASD-s

The cation exchange resin SDV was prepared by sulfonating the copolymer with sulfuric acid (sp. gr. 1.84) in the presence of a catalyst at 80-85° for four hours.

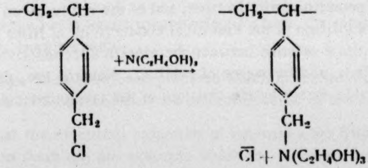
The cation-exchange resin SF was synthesized by phosphorylation of the same copolymer with excess (three moles per styrene link) phosphorus trichloride in the presence of aluminum trichloride (one mole per styrene link). Phosphorylation was carried out for 10 hours at the boiling point of phosphorus trichloride. Breakdown of the intermediate complex was carried out with water: oxidation of the copolymer was carried out by heating the phosphorylated copolymer with nitric acid



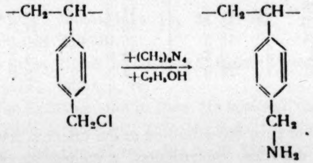
The cation-exchange resin KS was prepared by chloromethylation of the copolymer [14], with subsequent oxidation of the chloromethyl groups in the copolymer. Oxidation was effected by heating the chloromethylated copolymer with nitric acid at a temperature of 70-80° for eight hours:



The anion-exchange resin ASD-v was obtained by replacing the chlorine in the chloromethylated copolymer with triethanolamine. Amination was carried out by heating the chloromethylated copolymer with excess amine at 100° for six hours.



The anion-exchange resin ASD-s was prepared by replacing the chlorine atom in the chloromethylated copolymer of styrene and divinylbenzene, with a primary amine group; this was carried out by the action of the equivalent amount of hexamethylenetetramine at room temperature, with subsequent degradation of the intermediate compound by heating the copolymer with excess ethanol and hydrochloric acid at 60° for three hours.



The properties of the ion-exchange resins synthesized are given in Table 1. The same Table also contains data on the properties of the sulfonated cations exchange resins SBS-1 and SBS-2, and of the average basic anion exchange resin EDE-10P whose macromolecules have a different structure.

TABLE 1

Ion-exchange resin	Acid No. mg-eq/g	Basicity, mg-eq/g	Capacity in 0.1 N NaCl solution, mg-eq/g	Swelling coefficient in water
SDV	4.6	0	4.0	2.1
SF	3.6	0	3.8	1.6
KS	2.3	0	0	1.15
ASD-v	0	2.8	2.1	1.5
ASD-s	0	4.0	0	1.45
SBS-1	2.6	0	2.4	1.25
SBS-2	3.8	0	3.7	2.2
EDE-10P	0	7.5	1.0	2.0

In order to characterize the extent to which the ion-exchange resins ionize at different pH values, results are given in Fig. 1 which were obtained during the potentiometric titration of the cation-exchange resins SDV, SF, SBS-1, KS, while potentiometric titration curves for the anion exchange resins ASD-v, ASD-s, and EDE-10P are given in Fig. 2.

The ion-exchange films were prepared by grinding the cation and anion exchange resins into a powder, they were prepared, respectively, in the hydrogen and hydroxyl forms and mixed with the unfilled raw rubber mixture based on chloropropene rubber. The mixing was carried out in rollers at a temperature not exceeding 30°. The amount of the resin used in all cases was 70% of the total mass. The mixture was calendered until thin films were obtained, the films were then compressed and at the same time vulcanized between heated slabs. Pressing was carried out under a pressure of 10-15 kg/cm^2 and a temperature of 80-100° for 20 minutes.* The properties of the ion-exchange films prepared are indicated in Table 2.

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* N. V. Anashkina and V. M. Vinogradov participated in the preparation and study of the ion-exchange films.

Analysis of the results of potentiometric titration, and of the results given in the tables permits one to bring out some regularities. Comparison of the electrical conductivity of films made from SBS-1, SBS-2, and SDV indicates that there is a definite relation between the electrical conductivity of the film and the concentration of ionogenic groups in it, and its degree of swelling. Nevertheless, this relation is not well-defined and is determined to a considerable extent by the structure of the macromolecules of the ion-exchange resin chosen.

TABLE 2

Ion-exchange film	Thickness	Swelling in H_2O, % increase in thickness	Stability limit on stretching, kg/cm²		Specific volume resistance in 0.1 N NaCl, ohm/cm
			dry	swollen	
P-SDV	0.3	37	16.5	8.0	478
P-SBS-1	0.32	18.3	32.0	28.0	1250
P-SBS-2	0.3	22.8	26.0	17.0	430
P-SF	0.28	20.4	17.5	14.0	204
P-KS	0.29	17.0	45.0	47.0	11 680
P-ASD-v	0.34	18.5	25.0	20.0	828
P-ASD-s	0.3	6.8	9.0	4.5	9988
P-EDE-10P	0.31	28.0	7.5	5.0	473

It has not been found possible to give due attention to the effect of the structure of the ion-exchange resin on the electrical properties of the film. Nevertheless, a comparison of the properties of films P-SBS-2 and P-SDV shows that it should be possible to increase the electrical permeability of the diaphragms further by modifying the structure of the ion exchange resin.

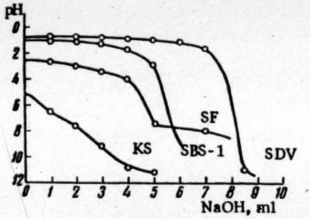

Fig. 1

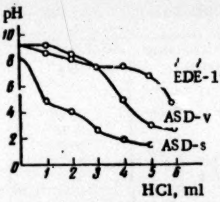

Fig. 2

When the structure of the ion-exchange resin is the same it is easy to follow the relation between the volume resistance of the ion-exchange films and the extent to which the ionogenic groups in the resin are ionized. But, even in this case, comparison of ion-exchange resins with different structures destroys the repeatedly established proportionality in this relationship (e.g., ASD-v and EDE-10P or SBS-2 and SF).

Despite the fact that the concentration of the basic groups in the ion-exchange resin ASD-v is 2.5 times less than that in EDE-10P, its resistance is only twice as much as that of EDE-10P. Preparation of anion exchange resins of the type ASD-v with a higher content of ionogenic groups, and the choice of a more suitable structure for its macromolecules, should enable one to prepare anion exchange resins with the minimum resistance.

The electrical properties of cation exchange films containing phosphate groups have not been described in the literature. Meanwhile, research has shown that films of SF may be of considerable interest for electroion exchange setups, since they have a resistance which is only half that of films of the cation exchange resins SDV and SBS-2. Films containing carboxyl groups and primary amine groups (ion exchange resins KS and ASD-s) have a high resistance and are not suitable as diaphragms in electroion exchange setups.

SUMMARY

Monofunctional ion exchange resins whose macromolecules have the same structure, but which contain different ionogenic groups, have been prepared.

Heterogeneous ion exchange films have been prepared which differ from each other in the type of ionogenic group they contain, or in the structure of the macromolecule of the ion-exchange resin.

It has been established that the electrical properties of ion-exchange films depend not only on the concentration of ionogenic groups in them and the extent to which the latter are ionized, but also on the structure of the macromolecules of the ion-exchange resin chosen.

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AN EXPERIMENT IN THE USE OF A PLASMA GENERATOR FOR THE SPECTROGRAPHIC ANALYSIS OF SILICATES

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Recently, Margoshes and Scribner [1], and, independently of them, the authors of the present article [2] turned their attention to the expediency of using a plasma generator [3] as a new, efficient spectrum excitation source, and showed that by means of this source it is possible to achieve a significant increase in the accuracy of the spectrochemical determination of a large number of elements. The present article is devoted to the first results obtained when this source was used for the spectrographic analysis of silicates.

The Design of a Plasma Generator for the Analysis of Solutions. The external appearance and the constructional details of the plasma generator are shown in Fig. 1. The generator consists of a hollow base 1 and a cover 2 cooled by water which passes through a sleeve 3. Between the base and the cover is fitted an insulating glass ring 4. There is an opening in the center of the cover, into which, on thread is fitted a capsule 5 into which a graphite electrode 6 has been fitted beforehand. The cover is fastened by means of an angle bracket 7, a joint 8, and a screw 9 to the triangular plateau 10. In order to change electrodes the cover can be lifted upward by turning the screw around the axis. The base also has an opening with a thread for fitting a gadget carrying the lower carbon electrode 11 to the cell. This gadget consists of a molded socket 12, on the outer surface of which there is a thread; and the socket 13 in which is fitted a bearing 14 with an opening for passing the gas and for setting up the lower electrode. In addition, by means of a socket 15, washer 16, a rubber stopper 17, and spring 18, a separator is fitted to the base of the generator. An arc discharge is excited by direct (short) circuiting of the electrodes, for which purpose the separator 19 and the sleeve 15 connected to it are lifted upward. After the discharge has been excited, all the movable system is returned by means of spring 18 to its original position. Rubber gaskets 20 are used to ensure that the generator is hermetically sealed. For convenience in dismantling the generator, fastening of the cover, and of the base with the glass ring, was achieved by means of three special dowels 21 with molded screws 22. In order to form the aerosol, roughly the same type of glass sprayer fitted with a system of separators as that used in flame photometers is used. In order to lower the extent of condensation of the aerosol on the inner cell walls, a quartz ring 23 is fitted. The arc is fed from a mercury rectifier with rectified current at 270 volt. Cooling gas (argon) is supplied to the generator through the sprayer from a cylinder. The gas pressure is measured with a manometer. A plasma generator of this design enabled us to obtain a plasma stream, bright white in color 40-50 mm long. The dimension of the inner cone* of the plasma stream amounted to 10 mm in length. On introducing water as an aerosol into the plasma, the stream acquired a red color, while the line 4340.5 A of excited hydrogen atoms appeared in the radiation spectrum.

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* We use this term arbitrarily by analogy with a flame.

The plasma generator was operated at different current densities and at different pressures of the cooling gas. The optimum conditions were found to be: current, 15-22 amp, and a pressure at the inlet into the sprayer of 0.8-1.2 atm. At lower current densities and at lower gas pressures, ejection of the plasma stream was difficult, and there was observed a break in the sprayer operation. Higher values of current and gas pressure led to overheating of the generator walls and to extinction of the arc discharge.

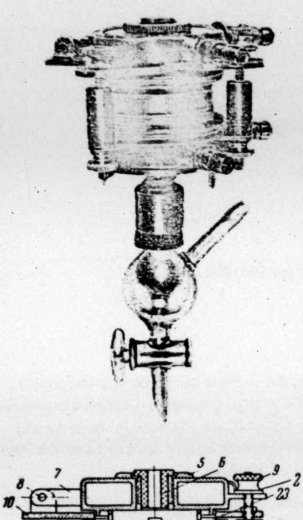

Fig. 1. External appearance and constructional details of the plasma generator used for analysis of solutions.

In a previous communication [2] experimental data were published which enable one to assess the way in which the atoms of certain elements pass into the plasma, and to assess the regularities in the distribution of the excited atoms and ions in the plasma stream. Further work on a large number of elements has shown that on introducing the test solution into the plasma in the form of an aerosol, it is possible to exclude completely the phenomenon of fractional distillation of the elements, and to achieve a high degree of uniformity in the passage of the elements into the plasma stream during analysis (Fig. 2). In Fig. 2, the curves illustrating the passage of Si, Ti, Al, and Fe, obtained during testing of the source, are compared with the corresponding curves obtained during evaporation of the same elements from the sample in the form of a powder in a dc arc and in an impulse arc [4]. It was observed that the degree of uniformity in the passage of the material into the plasma stream could be increased further by adding a small amount of a standard to the test solutions. At the same time, this technique favors an essential increase in the intensity of the whole spectrum, it is, however, accompanied also by some increase in background intensity. In Fig. 3, is shown a group of curves which demonstrate the blackening distribution of the lines of the excited atoms and ions of different elements along the plasma stream. As is evident, for atoms or ions of elements which have low or medium ionization potentials, the curves for changes in blackening of the lines along the plasma stream are characterized by the presence of a distinct maximum. It is located within the limits of the inner cone of the plasma stream, possessing the highest temperature, while the nearer to its base the higher the value of the excitation potential of the line. For lines with the highest excitation potentials, the maximum on the distribution curves, accordingly, almost coincide with the abscissa, i.e., with the base of the plasma stream. Beyond the maximum the paths taken by the distribution curves of the excited atoms and ions along the plasma stream almost coincide for all the elements, and are very near to straight lines. The only exceptions are those elements with very low ionization potentials; for these, at the tip of the plasma stream; there is observed a slower drop in the curve for changes in blackening of the line with distance, than for elements with average values of the excitation potentials.

The high stability of the operation of the generator, the uniformity with which various elements pass into the plasma, and the high degree of similarity in the nature of the distribution of their excited atoms and ions along the plasma stream, ensure high accuracy and reproducibility for spectrographic determination. Moreover, during spectrographic silicate analysis in solution, one can count on appreciably weakening, or avoidance of interference from the mutual effect of the elements on each other, and interference from the base material, and one can analyze samples by means of synthetic standards.

Technique for the Analysis of Silicates. Quantitative determination of the nine basic components of silicate (Si, Ti, Al, Fe, Ca, Mg, Mn, Na, K) is carried out on one aliquot, the contents of the various elements ranging from 0.5 to 80 %. Dissolution of the test material, and determination of the elements are carried out in two stages. During the first stage silicic acid is removed and it is then quantitatively determined gravimetrically [5, 6], while during the second stage the filtrate is analyzed for Ti, Al, Fe, Ca, Mg, Mn, K, and Na.

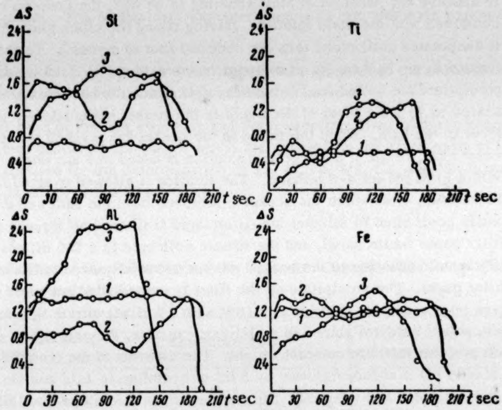

Fig. 2. Change in blackening of the lines ($\Delta S = S_{line} - S_{background}$) of different elements with time, during excitation in the plasma stream of a plasma generator (1), in the plasma of an impulse arc (2), and in a dc arc (3). Silicon on the basis of the 2514 A line, titanium on the basis of the 3653.5 A line, aluminum on the basis of the 3944.0 line and iron on the basis of the 2599.4 A line. The relative arrangement of the curves on the graph is arbitrary.

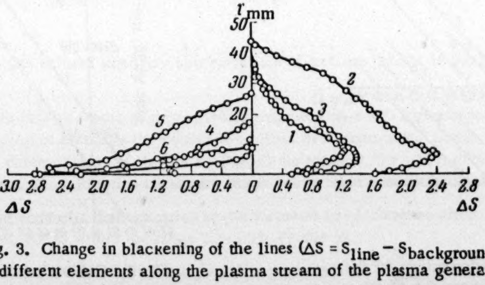

Fig. 3. Change in blackening of the lines ($\Delta S = S_{line} - S_{background}$) of different elements along the plasma stream of the plasma generator. 1) On the basis of the line Na I 588.9 (excitation potential, 3.75 ev); 2) on the basis of the line Al I 3944 (4.02 ev); 3) on the basis of the line Fe I 3020 (4.19 ev); 4) on the basis of the line Fe II 2382.0 (4.82 ev); 5) on the basis of the line Mg II 2802.7 (8.8 ev); 6) on the basis of the line C I 2478.6; . 7) on the basis of the line H, 4340.5.

a) Dissolution of the Sample and Determination of SiO_2. A 1 g aliquot of the test silicate is mixed in a platinum crucible with six times its amount of lithium carbonate and is fused with the latter. After cooling, the melt is transferred to a 300 ml beaker, the crucible being rinsed with small portions of hot water. Having covered the beaker with a clock glass, 20 ml of hydrochloric acid sp. gr 1.19 is gradually added through a fine nozzle, and the whole heated on a water bath until the melt has decomposed completely. A little hydrochloric acid sp. gr. 1.19 is added to the crucible in which the fusion was carried out, and the crucible heated in order to dissolve any particles of melt adhering to its side, the contents of the crucible are combined with the main solution. Having rinsed the clock glass, the solution in the beaker is evaporated until moist salts are obtained (not to dryness). To the salts which have formed in the beaker, 30 ml of hydrochloric acid sp. gr. 1.19 is added. Solution plus precipitate are boiled for 10 minutes, after which the beaker is placed on a water bath heated to 70°, the level of the liquid in the beaker being slightly lower than the water level in the bath. When the liquid in the beaker has reached the temperature of the water bath, 10 ml of a 1% gelatin solution is added and the whole thoroughly mixed with a glass rod for 4-5 minutes. The solution is allowed to stand on the bath for a further 10 minutes, after which the beaker is removed from the bath and the liquid allowed to get really cool; after 10 minutes the silicic acid is filtered off through a medium porosity filter paper (white band), and the filtrate collected in a 200 ml beaker. Any particles of silicic acid adhering to the beaker walls are carefully wiped off with pieces of ashless filter paper. The precipitate on the filter is washed with hot water until the washings give no reaction for chloride ions (test with 1% silver nitrate solution). The filter paper plus silicic acid are placed in a platinum crucible, they are dried, carefully ashed, and then calcined in an oven at 1000-1100° to constant weight. The contents of the crucible are washed with water, a few drops of sulfuric acid (1:1) is added, followed by 5 ml of hydrofluoric acid and the whole evaporated to dryness. The dry residue is calcined and weighed. The residue in the crucible is fused with 100 mg of lithium carbonate and the melt treated with hot water acidified with hydrochloric acid. The solution obtained is combined with the filtrate left after removal of silicic acid. The filtrate is evaporated to approximately 50 ml and is transferred to a 100 ml standard flask, 6 ml of molybdenum solution is added, the concentration of the latter being 20 mg/ml, and 10 ml of standard; the volume is finally made up to the mark with water.

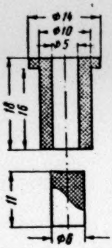

Fig. 4. Shape and size of the electrodes.

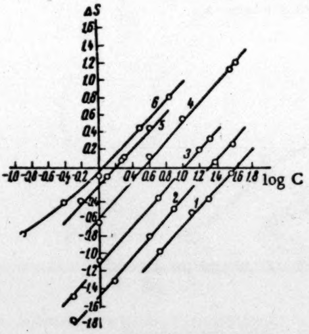

Fig. 5. Calibration curves for the determination of Mg (1), Fe (2), Al (3), Ca (4), Ti (5), Mn (6).

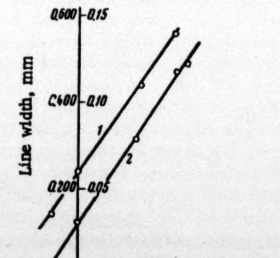

Fig. 6. Calibration curves for the determination of K (2) and Na (1) by the spectral line width method.

b) Spectrographic Analysis of the Filtrate. The filtrate obtained after removing the silicic acid, or a standard solution, converted by means of the sprayer into an aerosol through the system of separators, is transported along rubber tubing into the inner space of the plasma generator, and then into the plasma stream. The optimum gas pressure at the inlet into the sprayer is 1 atm. Under these conditions the amount of solution used up is 3-4 ml/min. The current is 20 amps. The shape and size of the electrodes are shown in Fig. 4. The interelectrode distance is 4 mm. Both electrodes are replaced after taking three successive spectra, whether of standards or test sample.

Light from the part of the plasma stream located at a distance of about 8-10 mm from the generator nozzle is projected through a one lens system onto the slit of ISP-22 and ISP-51 spectrographs (camera with $f = 270$ mm). The spectra are photographed on "Spectrographic" plates type II, sensitivity 22 GOST units and on Infrachrome 760 plates. The preliminary exposure time is 15 sec, the main exposure time 60 sec. D-19 developer is used.

Standard solutions, obtained by mixing the appropriate amounts of the chlorides of the test elements and the reference elements, are used for constructing calibration curves.

The analytical lines of the test elements and the appropriate lines of the reference element are given in Table 1. The optimum concentration ranges which are covered by the given pairs of lines are also included. The reference element used for the determination of Ti, Al, Fe, Mg, Ca, and Mn is molybdenum, while lithium is used for the determination of the alkali metals.

TABLE 1

Analytical Lines of the Elements and the Optimum Concentration Range During Determination of These Elements in Silicates

Line of the test element		Reference line	Optimum concentration range of the test element, %
Ti I	3653.5	Mo 3680.6 Mo 3208.8	0.1— 2.5
Al I	3944.0	Mo 3208.8	0.5—40.0
Fe II	2599.4	Mo 2616.8 Mo 3208.8	0.5—40.0
Ca I	3630.8	Mo 3680.6	3.0—40.0
	4226.7	Mo 4277.2*	0.1— 3.0
Mg II	2779.8 2776.7 2802.7	Mo 2775.4	4.0—40.0 0.1— 4.0
Mn	2801.1	Mo 2775.4	0.1—20.0
Na I	5889.9	Mo 4760.2	0.5—12.0
	5895.9	Li 6707.8	
K I	7664.9	Mo 4760.2	0.5—17.0
	7798.9	Li 6707.8	

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* This line can be used when low concentrations of iron are present in the test sample.

The spectrograms obtained were photometrically measured on a MF-2 microphotometer. During determination of the first group of elements the calibration curves were constructed within the coordinates $\Delta S - \log C$ (Fig. 5), while for the determination of Na and K (Fig. 6) the spectral line width method was used [7, 8]. As is evident, in both cases, the calibration curves are linear over a wide concentration range.

The mean square error of a determination of the elements (σ_{Σ}) obtained after treating the results of 50 parallel determinations, varies within the range 2.5-3.5% (Table 2).

When, using Nalimov's data [9], it is assumed that the values of $\sigma_{\text{phot.}}$ and σ_{plate} should be of the order of 1.7 and 2.7%, respectively, for the photographic materials and the developing conditions we used, then the square error related to instability in the operation of the generator under our conditions does not exceed 1.5%. The correctness of the experimental results obtained by the method described was checked by comparing the results of determining the elements by a chemical method and by the spectrographic method (Table 3).

As is evident, the extent to which the experimental results obtained by the two methods agree is completely satisfactory. The question of the mutual influence of the elements on each other during their spectrographic determination by the method described was not specially studied in the work described here. Nevertheless, bearing in mind the results of previous work in this field [7, 8] and the well-known fact that these mutual influences are strongly weakened in work with solutions which are far from being saturated, it may be accepted with a high degree of confidence that such an effect will be almost nonexistent.

TABLE 2

Comparison of Experimental Errors During Determination of Elements by Means of Various Excitation Sources

Source	Standard error of a determination							
	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	TiO_2	Na_2O	K_2O
dc or ac arcs	3.4	6.1	4.5	6.7	—	—	6.0	5.0
Impulse arc	2.7	2.5	2.8	3.3	3.5	3.4	3.5	3.2
Plasma generator	3.2	2.7	2.9	3.4	2.8	3.0	2.8	2.6

TABLE 3

Comparison of the Results of Chemical and Spectrographic Determination of Elements

Sample	1		2		3		4	
Components	Found, %							
	*A	*B	*A	*B	*A	*B	*A	*B
TiO_2	0.42	0.56	0.62	0.61	1.17	1.15	0.76	0.72
Al_2O_3	15.76	15.60	6.85	6.93	18.12	18.63	6.54	6.46
Fe_2O_3	4.19	4.3	3.53	3.54	7.46	7.76	3.32	3.29
CaO	4.77	4.67	0.38	0.41	3.14	3.06	0.15	0.15
MgO	1.92	2.05	0.40	0.41	3.95	3.98	0.52	0.51
MnO	0.1	0.1	0.07	0.07	0.06	0.06	0.28	0.28
Na_2O	5.02	4.95	0.08	0.10	0.01	Not det.	0.01	Not det.
K_2O	1.99	2.08	0.36	0.38	6.55	6.35	0.94	0.92

* A = Chemical method, * B = Spectrographic method.

The authors wish to thank N. I. Korolev for help in the experimental work.

SUMMARY

A design for a plasma generator which can be used for the analysis of solutions is described; new results have been obtained which indicate a high degree of uniformity in the passage of elements into the source plasma, and which indicate the characteristic nature of the distribution of excited atoms and ions of certain elements (Na, Al, Fe, Mg, Si, C, and H) in the plasma stream.

A new spectrochemical method has been developed for the quantitative determination of from 0.5 to 80% of Si, Ti, Al, Fe, Ca, Mg, Mn, Na, and K in silicates, with an average square error of 2.5-3.5%.

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THE USE OF THIOSEMICARBAZIDE AND ITS PHENYL DERIVATIVES IN ANALYTICAL CHEMISTRY.

SPOT AND NONDESTRUCTIVE TESTS FOR COPPER

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Thiosemicarbazide and its phenyl derivatives* are used in analytical chemistry for the detection and determination of certain metals [1-8]. Earlier [2] one of us developed a method for the photocolorimetric determination of copper by means of thiosemicarbazide. We thought it would be interesting to establish the effect of the introduction of various substituents into the thiosemicarbazide molecule, on the selectivity and sensitivity of this reaction. One should expect that the nature of the way in which the reaction proceeds between copper ions and thiosemicarbazide on the one hand, and between copper ions and the substituted thiosemicarbazides on the other, will differ somewhat as a result of the replacement of the hydrogen in the molecule of the reagent by phenyl and other groups. It might be expected in such a case that the sensitivity and selectivity of the reaction in the second case will be greater than in the first. The acidity of the medium might also be significant, since, depending on the latter, various tautomeric forms of the compounds of thiosemicarbazide and its derivatives may be formed with copper ions.

In this connection we therefore studied 2-methyl-, 4-methyl-, 2,4-dimethyl-, 1-phenyl-, 4-phenyl-, and 1,4-diphenylthiosemicarbazides as reagents for copper.

Unsubstituted thiosemicarbazide gives with copper ions at pH 0-4 in nitric, hydrochloric, and sulfuric acid solutions, a dark blue colored compound which is soluble in water and sparingly soluble in organic solvents. The alkyl derivatives of thiosemicarbazide also give blue colored compounds under the same conditions, but the sensitivity of the reaction of these derivatives with copper is no higher than that of thiosemicarbazide itself. At pH 4-12, the alkyl substituted derivatives of thiosemicarbazide, like thiosemicarbazide itself, form yellow-brown colored compounds with copper ions. We did not study the alkyl substituted derivatives of thiosemicarbazide further.

A chemical analysis of the products formed by the interaction of thiosemicarbazide with copper ions in acid and alkaline media showed that their composition is not the same. For a compound isolated earlier by one of us [2] from an acid solution, the copper content was found to be 18.6% instead of the theoretical value of 18.5%. Physicochemical studies showed that the ratio of copper to thiosemicarbazide in this compound was 1 : 2, while magnetometric measurements established the presence of cupric ions only. Appropriate qualitative reactions and chromatographic experiments showed that this compound is an electrolyte. The product formed by the interaction of thiosemicarbazide with copper ions in alkaline media is not an individual material. The magnetic moment of this compound corresponds to divalent copper and is 1.46 M_0 (for univalent copper it is 0, while for divalent copper which is paramagnetic, it is 1.75 M_0). The copper content of this product was found to be 58.8% and the sulfur content 41.6%. The product obtained is insoluble in water, and, apparently, is a complex nonelectrolyte. The composition of the compound formed by the interaction of thiosemicarbazide with copper ions in an alkaline medium was not studied by physicochemical methods.

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* We only learned of the detection and determination of copper by 1,4-diphenyl thiosemicarbazide [7] when the work described here had been completed. Since the results we have obtained extend and supplement available information, we decided that it would be useful to publish them.

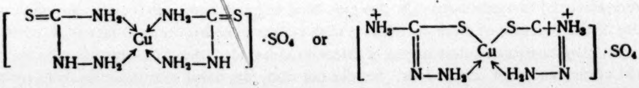
1-Phenylthiosemicarbazide, which was suggested as a reagent for copper by Naito and Takahashi [5], gives with copper ions at pH 0-4, a blue colored compound, while at higher pH values the compound formed is green in color. It behaves up to a certain extent in the same way as thiosemicarbazide. The compound formed between 1-phenylthiosemicarbazide and copper ions in an acid medium, is sparingly soluble in water, and is fairly soluble in acetic acid and organic solvents.

4-Phenylthiosemicarbazide forms a green colored compound with copper ions. In very dilute solutions the green color of this compound is preserved over a wide pH range (0-12). In more concentrated solutions, at pH greater than 2, a precipitate of pale violet color is formed, which is insoluble in water and ethanol, and sparingly soluble in organic solvents and mineral acids.

Using the isomolar series method it was shown that in acid media, 1-phenylthiosemicarbazide and 4-phenylthiosemicarbazide react with copper ions in the molar ratio of 1 : 2. These compounds were not analyzed chemically.

1,4-Diphenylthiosemicarbazide at pH 0-12, forms a green colored compound with copper ions. This compound is sparingly soluble in water, but is readily soluble in organic solvents: benzene, chloroform, carbon tetrachloride, ethyl, amyl, and isoamyl alcohols, toluene, and acetone. The compounds formed between 1,4-diphenylthiosemicarbazide with copper ions in acid (pH 1-2) and alkaline (pH 9-10) solutions were isolated in a crystalline state, and proved to be identical. When these compounds were prepared from sulfuric acid solutions, it was found that they did not contain the sulfate ions, this was proved by the absence of a precipitate on testing with barium nitrate. They were also free from Cl^- and NO_3^- when prepared from hydrochloric and nitric acid solutions. Apparently, 1,4-diphenylthiosemicarbazide forms only one compound with copper ions, this compound being probably a complex nonelectrolyte. Chemical analysis established that the copper content of this compound is 13.5% while the sulfur content is 12.02%; these figures tie in most closely with the formula $Cu(C_{13}H_{12}N_3S_2)$ (calculated values: 11.6% Cu and 11.67% S). This ratio was confirmed by measuring the optical density of isomolar mixtures of aqueous-alcoholic solutions of 1,4-diphenylthiosemicarbazide and aqueous solutions of cupric sulfate, and also of mixtures of solutions with varying concentrations of one of the components, on a SF-4 spectrophotometer at varying wavelengths.

The sulfate of cupric thiosemicarbazidinate, isolated from an acid solution, may have the following structure



In order to choose between one structural formula and the other, infrared absorption spectra were taken of thiosemicarbazide, 1,4-diphenylthiosemicarbazide and of their compounds with copper, on a IKS-12 spectrophotometer, in the region characteristic for the absorption frequency of the thioureide group $-N=C=S$. On comparing these spectra it was established that bands with a frequency of 1540 cm^{-1} are present in the spectra of thiosemicarbazide and 1,4-diphenylthiosemicarbazide, these bands obviously belong to the thioureide group (according to published data the characteristic frequency of this group lies within the range 1470-1600 cm^{-1}). The absorption spectra of the compounds of thiosemicarbazide and 1,4-diphenylthiosemicarbazide with copper do not contain any bands in the region indicated. The disappearance of the absorption bands indicated testifies to some extent that the sulfur atom participates in the formation of the bond with the copper ion.*

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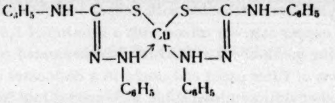
* The infrared absorption spectra of thiosemicarbazide and 1,4-diphenylthiosemicarbazide, and also of their compounds with copper, were taken by L. F. Trefilova.

Taking into account all that has been said above, and also the opinions of Kuznetsov [9], Irving [10], Toropova [12] and other research workers on the structure of complex compounds of metallic ions with organic compounds containing sulfur, the second structural formula given above would appear to be most likely one for cupric thiosemicarbazadinate sulfate.

Formulas analogous to that of cupric thiosemicarbazadinate sulfate can, presumably, be ascribed to the compounds of 1-phenyl- and 4-phenylthiosemicarbazide with copper ions when isolated from acid solutions.

The properties and composition of the compounds of thiosemicarbazide, 1-phenylthiosemicarbazide, and 4-phenylthiosemicarbazide with copper ions, isolated from alkaline solutions were not studied.

As for the compound of 1,4-diphenylthiosemicarbazide with copper ions, it is presumably a complex nonelectrolyte (inner complex compounds). The properties of this compound are in good agreement with the formula:



1-Phenyl, 4-phenyl-, and 1,4-diphenylthiosemicarbazides, in view of the presence in their molecules of phenyl groups in addition to the thio group, could presumably be more sensitive reagents for copper ions than thiosemicarbazide and semicarbazide. Experiments which were carried out showed that in fact the sensitivity of reactions involving the phenyl substituted thiosemicarbazides is higher than that with thiosemicarbazide and semicarbazide. Using organic solvents for extracting the compounds formed, the sensitivity is $5.0 \cdot 10^{-8}$ g/ml for 1,4-diphenylthiosemicarbazide, $5.0 \cdot 10^{-6}$ g/ml for 4-phenylthiosemicarbazide, and $5.0 \cdot 10^{-7}$ g/ml for 1-phenylthiosemicarbazide. The sensitivity of the analogous reactions with thiosemicarbazide and semicarbazide is $5.0 \cdot 10^{-6}$ and $5.0 \cdot 10^{-4}$ g/ml, respectively.

On adding a solution of thiosemicarbazide to a solution of copper semicarbazadinate, the color changes from light-blue to the blue-violet characteristic of copper thiosemicarbazadinate. By the action of 1-phenylthiosemicarbazide on a solution of copper thiosemicarbazadinate, the color changes into a dark-blue characteristic of copper 1-phenylthiosemicarbazadinate. On adding solutions of 4-phenylthiosemicarbazide or 1,4-diphenylthiosemicarbazide to a solution of copper 1-phenylthiosemicarbazadinate, the color changes to green characteristic for copper 4-phenyl- and 1,4-diphenylthiosemicarbazadinates (when a solution of the second reagent is used, and at a sufficiently high concentration of 1-phenylthiosemicarbazide in solution, a green precipitate is rapidly formed). On mixing a solution of sodium ethylenediaminetetracetate (EDTA-Na) with a solution of copper 1,4-diphenylthiosemicarbazidinate the green color slowly changes to a bright-blue, characteristic for copper ethylenediaminetetracetate.

On the basis of the results given above, it is possible to compile a practical series of copper carbazadinates, in which each of the preceding members is less stable than the subsequent member:

$$[\mathrm{Cu}\,(\mathrm{SC})_2]^{2+},\ [\mathrm{Cu}\,(\mathrm{TSC})_2]^{2+},\ \ [\mathrm{Cu}\,(1\text{-}\mathrm{FTSC})_2]^{2+},\ \ [\mathrm{Cu}\,(4\text{-}\mathrm{FTSC})_2]^{2+},\ [\mathrm{Cu}\,(1{,}4\text{-}\mathrm{DFTSC})_2]$$

1,4-Diphenylthiosemicarbazide gives stable, and, in some cases, sparingly soluble compounds, not only with copper, but also with silver, mercury, zinc, cadmium, iron, gold, platinum, palladium, iridium, rhodium, and ruthenium; only platinum of the noble metals forming a green colored compound. They are readily extracted by organic solvents, but the reaction of 1,4-diphenylthiosemicarbazide with the ions of these metals is less sensitive than its reaction with copper. Small amounts of the cations of the metals indicated do not interfere with detection of copper, large amounts depress the sensitivity of detection somewhat. Copper can be detected in the presence of silver and mercury at a ratio of Cu : Me = 1 : 1000, while in the presence of gold, palladium, ruthenium, osmium, rhodium, iridium, platinum and rhenium, copper can be detected at a ratio of Cu : Me = 1 : 30. Interference from large amounts of iron can be removed by using sodium fluoride or phosphate. The majority of anions, with the exception of intensely colored ones, does not interfere with copper detection. Concentrated nitric and perchloric acid destroy the compounds formed between metal ions and 1,4-diphenylthiosemicarbazide.

The listed properties of the inner complex compound formed during the interaction of cupric ions with 1,4-diphenylthiosemicarbazide favorably distinguish this reagent from thiosemicarbazide and 1-phenylthiosemicarbazide, and some other compounds which have been suggested for the detection and determination of copper.

Preparation of 1,4-Diphenylthiosemicarbazide and its Compound with Cupric Ions. Walther's method [13], somewhat improved by us, was used for synthesizing 1,4-diphenylthiosemicarbazide.

6.9 g (0.03 mole) of thiosemicarbazide (diphenylthiourea) and 4 ml (4.3 g or 0.04 mole) of phenylhydrazine were boiled in 50 ml of alcohol in a flask fitted with a reflux condenser for four hours. After cooling the reaction mixture, the precipitate which separated out was filtered and washed with alcohol. The 1,4-diphenylthiosemicarbazide prepared in this way appeared as shining prisms with a m. p. of 177° (published m. p. 176-177°). Yield 6.7 g (92% of theory).

The compound of 1,4-diphenylthiosemicarbazide with copper was obtained both in acid and in alkaline solutions. An aqueous solution of a copper salt was mixed with a solution of 1,4-diphenylthiosemicarbazide in concentrated acetic acid. The shining green crystals which thereby separated out were filtered off, washed with alcohol and dried between sheets of filter paper and stored in a desiccator over sulfuric acid. During isolation of the compound of 1,4-diphenylthiosemicarbazide with copper ions from an alkaline solution, an alcoholic solution of 1,4-diphenylthiosemicarbazide was added to an aqueous-ammonia solution of a copper salt; the subsequent procedure was the same as in the previous instance.

Methods of Detecting Copper by Means of 1-Phenyl- and 1,4-Diphenylthiosemicarbazide. To 0.2-0.3 ml of the test solution is added 1-2 ml of a saturated alcoholic or acetic acid solution of reagent (1-phenylthiosemicarbazide or 1,4-diphenylthiosemicarbazide) and the whole mixed. If, at this stage a precipitate is formed, the volume of reagent added is increased 2-3 times, or the corresponding amount of ethanol is added. The appearance of a green color (when 1,4-diphenylthiosemicarbazide is used) or a blue color (when 1-phenylthiosemicarbazide is used) testifies to the presence of copper in the test solution. Under these conditions, the sensitivity of the detection of copper in the presence of other cations amounts to $5.0 \cdot 10^{-6}$ g/ml for 1,4-diphenylthiosemicarbazide and $5.0 \cdot 10^{-5}$ g/ml for 1-phenylthiosemicarbazide.

Spot Detection of Copper in the presence of other cations is carried out as follows. 0.01-0.005 ml of test solution is placed by means of a capillary on a sheet of filter paper. 0.03-0.06 ml of reagent solution is placed by means of another capillary in the center of the still moist spot of test solution. When copper is present a green ring is formed between the center and the periphery of the spot. When the test solution contains mercury and gold a large excess of reagent must be used, this is done by putting two or three spots of reagent solution on the center of the moist spot. In this case, in addition to the green ring, a brown color appears at the spot center; this means that it is possible to detect copper, mercury, and gold, simultaneously. The sensitivity of the detection of copper in the presence of the other cations by the spot technique, using 1,4-diphenylthiosemicarbazide, is $6.0 \cdot 10^{-7}$ g/ml, while in the absence of the cations, the sensitivity is $1.0 \cdot 10^{-7}$ g/ml.

Nondestructive Detection of Copper by means of 1,4-diphenylthiosemicarbazide was carried out on zinc, nickel, ferrous, and gold alloys. On the surface of the alloys which has been cleaned beforehand is placed 2-3 drops of nitric acid (1:1) for zinc and ferrous alloys, or the same amount of a mixture of nitric and hydrochloric acids (1:1) for gold alloys. After the reaction has ceased, the solution on the alloy's surface is transferred to a porcelain crucible or basin. The alloy surface is washed with 2-3 drops of water and the wash water combined with the solution in the crucible. 1-2 drops of nitric acid is added to the solution in the crucible and the whole evaporated almost to dryness on a hot plate. To the residue is added 1-2 drops of hydrochloric acid and the volume of the solution made up to 1-2 ml with water. The solution is transferred to a test tube and 1-2 ml of reagent solution added. When a precipitate forms, 1-2 ml of ethanol is added. When copper is present a green color is formed.

During analysis of ferrous alloys, iron is masked by addition of sodium fluoride, while during the analysis of nickel alloys the solution is diluted with water to weaken the green color of the nickel salts. The test materials used for this study were zinc alloys containing 0.5 and 0.94% copper, a nickel alloy containing 0.54% copper, a carbon steel containing 0.33% copper, and a gold alloy containing 30.3% copper.

We wish to thank I. Ya. Postovskii for valuable advice in carrying out the work described here.

SUMMARY

A study has been made of the reaction of copper ions with certain substituted thiosemicarbazides.

Structural formulas are suggested for the compounds of copper with thiosemicarbazide and 1,4-diphenylthiosemicarbazide.

Optimum conditions have been established for carrying out the reactions with phenyl substituted derivatives of thiosemicarbazide, and the sensitivity of these reactions have been determined in pure solutions of copper salts, and in the presence of other elements.

Methods have been developed for detecting copper in zinc, nickel, gold, and ferrous alloys.

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SEPARATION AND DETERMINATION OF GALLIUM BY MEANS OF DIANTIPYRYLPROPYLMETHANE

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For the determination of comparatively large amounts of gallium, the latter is usually precipitated with ammonia, ammonium sulfite, camphoric acid, cupferron, and some other reagents, and it is finally weighed as Ga_2O_3 [1]. As a rule, the precipitates formed under these conditions are difficult to filter. In addition, many of the forms in which this element is weighed have unfavorable conversion factors. Other methods of precipitating gallium, e.g., in the form of its ferrocyanide, 8-hydroxyquinolate $(C_9H_6ON)_3Ga$, possess low selectivity and are only of importance for the determination of gallium in its pure salts, or after its separation, e.g., by extraction with diethyl ether from 5-6 M HCl.

Gallium is extracted in the form of basic compounds $HGaCl_4 \cdot x\, Org$ (where Org is the molecule of an oxygen-containing organic solvent).

The aim of the work described here, was to carry out a systematic study of the possibility of using precipitation of gallium by means of diantipyrylpropylmethane, for the separation and quantitative determination of this element. Diantipyrylpropylmethane has been used earlier [2] for the gravimetric determination of thallium in the presence of many elements including zinc, cadmium, copper, indium, and aluminum. Interference on the part of gallium was noted at the time.

Experiments showed that gallium starts to be precipitated by diantipyrylpropylmethane from 3 M HCl, it is precipitated quantitatively from 5.5-6 M HCl. Diantipyrylmethane and diantipyrylmethylmethane do not precipitate gallium quantitatively from hydrochloric acid solutions.

In order to determine the composition of the compound which is formed in hydrochloric acid solutions (6 M HCl) of gallium salts on adding diantipyrylpropylmethane, the precipitate obtained was filtered off and recrystallized from acetone; during this process the material separated out in the form of a colorless oily liquid which slowly crystallized on standing. Chlorine was determined by precipitation with silver nitrate from an aqueous-acetone solution, and weighing as AgCl, while gallium was determined by complexonometric titration with 1-(2-pyridylazo)-2-naphthol as indicator. In this latter instance an aliquot of the material was dissolved in a mixture of acetone and water (1:10), 2-3 ml of a 5% solution of tartaric acid was added, this was followed by ammonium acetate until the pH was 4.5-5, the solution was heated to 70-80° and gallium titrated with 0.01 M sodium ethylenediaminetetracetate in the presence of a few drops of a 0.1% solution of 1-(2-pyridylazo)-2-naphthol in methanol (until the color changed from red to pure yellow).

Analytical results showed that gallium is precipitated in the form of a compound whose composition corresponds to the formula $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$.

Found %: Cl 22.09, 21.76; Ga 10.84, 10.97. $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$. Calculated %: Cl 22.05; Ga 10.84.

In order to determine gallium quantitatively in the form of $C_{28}H_{30}O_2N_4 \cdot HGaCl_4$, to the test solution (we used a solution of gallium chloride obtained by dissolving an accurately weighed aliquot of spectrographically pure metallic gallium in hydrochloric acid) was added a 1% solution of diantipyrylpropylmethane in acetic acid (1 : 10), at the rate of 1 ml per mg of gallium, to the solution was then added, with stirring, an equal volume of hydrochloric acid (sp. gr. 1.19). Thus, the final hydrochloric acid concentration was 5.5-6 M. The white flocculent precipitate which formed, and which readily coagulated on stirring, was filtered off through a No. 3 glass crucible, and was washed with 6 M HCl containing 0.05% of the precipitant, and then with 6 M HCl. The precipitate was dried to constant weight at 100-110° (at this temperature the precipitate melts without decomposition). The conversion factor to gallium is 0.1084. The method gives results which are fully satisfactory with respect to accuracy. (Table 1); in addition, it is simple to carry out, and takes little time, since the precipitate is readily and rapidly filtered.

TABLE 1

Gravimetric Determination of Gallium in the Form of $C_{28}H_{30}O_2N_4 \cdot HGaCl_4$

Ga, mg		Error	
taken	found	mg	%
3.37	3.39	+0.02	+0.6
3.37	3.36	−0.01	−0.3
3.37	3.34	−0.03	−0.9
4.62	4.53	−0.09	−2.0
4.62	4.67	+0.05	+1.0
8.44	8.51	+0.07	+0.8
8.44	8.40	−0.04	−0.5
8.44	8.45	+0.01	−0.1
16.87	16.80	−0.07	−0.4
16.87	16.60	−0.27	−1.6

TABLE 2

Determination of Gallium in the Presence of Foreign Elements

Ga, taken, mg	Added, g	Ga found, mg	Error	
			mg	%
8.44	0.5 $CuSO_4 \cdot 5H_2O$	8.39	−0.05	−0.6
8.44	1.0 $CuSO_4 \cdot 5H_2O$	8.32	−0.12	−1.3
3.37	2.0 $Zn(CH_3COO)_2 \cdot 2H_2O$	3.44	+0.07	+2.0
3.37	3.0 $Zn(CH_3COO)_2 \cdot 2H_2O$	3.33	−0.04	−1.2
3.37	0.17 In	3.36	−0.01	−0.3
3.37	2.0 $Al(NO_3)_3 \cdot 9H_2O$	3.46	+0.09	+2.7
3.37	3.0 $Cd(NO_3)_2 \cdot 4H_2O$	3.40	+0.03	+0.9
3.37	4.5 $Cd(NO_3)_2 \cdot 4H_2O$	3.28	−0.09	−2.7
8.44	3.0 $Al(NO_3)_3 \cdot 9H_2O$	8.40	−0.04	−0.5
8.44	2.0 $Al(NO_3)_3 \cdot 9H_2O$	8.72	+0.28	+3.3
8.44	1.0 $Ni(NO_3)_2 \cdot 6H_2O$	8.36	−0.08	−1.0
3.37	2.0 $Ni(NO_3)_2 \cdot 6H_2O$	3.27	−0.10	−3.0
8.44	3.0 $MnCl_2 \cdot 4H_2O$	8.38	−0.06	−0.7
16.87	2.5 $MnCl_2 \cdot 4H_2O$	16.63	−0.24	−1.4
3.57	3.0 $MgCl_2 \cdot 6H_2O$	3.40	+0.03	+0.9

The suggested method possesses a high selectivity, since many elements do not interfere, they include: zinc, cadmium, copper, aluminum, nickel, manganese, magnesium, indium, cobalt, bismuth, and other elements (Table 2). Tl^{3+} and Fe^{3+} interfere.

Accordingly, the method can be used both for isolating gallium and separating it from accompanying elements. Trivalent iron must be reduced to the divalent state.

After gallium has been separated as $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$ its determination can be finished complexonometrically: the precipitate is filtered off, washed as indicated above, and then washed off the filter with water (50-70 ml), to the solution is added a few ml of a 5% tartaric acid solution, and the pH adjusted to about 5 with ammonium acetate; it is finally titrated, after warming it to 70-80°, in the presence of 1-(2-pyridylazo)-2-naphthol until the color of the solution turns from rose to yellow. The method gives satisfactory results (Table 3).

TABLE 3

Complexonometric Determination of Gallium After It Has Been Separated as $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$

Ga taken, mg	Added, g	Ga found, mg	Error, mg
3.37	—	3.36	—0.01
3.37	—	3.39	+0.02
8.44	—	8.37	—0.07
16.87	—	16.99	+0.12
8.44	0.25 $Bi(NO_3)_3 \cdot 5H_2O$	8.55	+0.11
8.44	0.50 $Bi(NO_3)_3 \cdot 5H_2O$	8.37	—0.07
8.44	1.0 $CoSO_4 \cdot 7H_2O$	8.43	—0.01
3.37	1.0 $CoSO_4 \cdot 7H_2O$	3.26	—0.11
3.37	0.437 In	3.36	—0.01
3.37	0.604 In	3.45	+0.08

SUMMARY

A description is given of a simple method for the isolation and separation of gallium from accompanying elements; the method is based on the precipitation of gallium . As $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$ from 5.5-6 M HCl by means of diantipyrylpropylmethane. Either a gravimetric finish can be used, in which the gallium is weighed as $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$, or the gallium can be determined complexonometrically, by titrating the gallium in the precipitate using 1-(2-pyridylazo)-2-naphthol as indicator.

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* Original Russian pagination. See C. B. translation.

DETERMINATION OF THE INDIUM CONTENT OF SPHALERITES BY RADIOACTIVATION ANALYSIS

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In papers [1-4] which have been published on the determination of indium in various samples by means of the activation method, radiochemical methods of separating indium from other elements are used in the main, these entail difficult and long operations. In this connection we have attempted to develop a technique for the determination of indium in sphalerites by direct measurement of the energy spectra of the test sample by means of a scintillation γ-spectrometer.

Development of quantitative methods for determining from hundredths to several tenths of a percent of indium in sphalerites is of practical importance. The basis of the technique is to obtain radioisotopes of indium by means of (n, γ) reactions. In Table 1 are given the energy characteristics of the elements which are present in sphalerites.

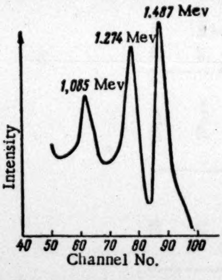

Fig. 1. The γ-radiation spectrum of the standard indium isotope-116.

The setup which we used consists of the following main parts: a) a vertical lead housing of special design (in which is found the spectrophotometer monocrystal NaI (Tl) which is 40 mm in diameter and 38 mm in length, and a photoelectronic multiplier type FEU-1S plus divider which is optically connected to it); b) a single channel amplitude analyzer with an amplifier; c) a counting setup; d) a stabilized high voltage rectifier.

The activated sample contained in a special cassette (cylindrical in shape) of organic glass was fitted onto the crystal in the lead housing. The electrical impulses from the photoelectronic multiplier passed (through a cathode repeater) onto the input of the amplifier. The analyzer channel was set up in the region of the photopeak with an energy of 1.273 Mev on the scale of the energy γ-spectrum of indium-116 (Fig. 1) for a channel width of 5 volt. The impulses were counted by a type PS-10,000 type counting setup. Prior to measurement of the activity of samples, the analyzer scale was calibrated on the basis of the energy photopeaks of the γ-radiation of the isotopes iodine-131, cobalt-60, cesium-137, and zinc-65. The energy scale of the analyzer in the energy range 0.3 to 1.5 Mev proved to be linear (Fig. 2).

In order to calculate the values of the activity of elements which enter into the composition of sphalerite, the results in Table 1 were used; their drop in activity curves (Fig. 3) were then constructed. The activity was calculated by means of the formula

$$\dot{I} = n\nu\sigma N\left(1 - e^{-\frac{0,693t}{T}}\right),$$

TABLE 1

Nuclear Characteristics of Elements Present in Sphalerite

Element	Isotope, distribution, %	Effective activation cross section by slow neutrons, b	Radioactive isotope	Half life period	Nature of the radiation β, γ	β-Radiation energy, Mev	γ-Radiation energy, mev	Yield of γ-quanta per 100 decays, %	Conc. of elements in the sample, %	Calc. activation I in arbitrary units for irradiation time of 3 hrs 30 min.	Log I
Sulfur	S^{34} (4.2)	0.26	S^{35}	87 days	β^-	0.167	none	—	33		
16^S	S^{36} (0.016)	0.14	S^{37}	5 min	β^-,	4.3 (10%) 1.6 (90%)	3.1	90.0		$2 \cdot 10^2$	2.9956
Zinc	Zn^{64} (48.9)	0.5	Zn^{65}	250 days	β^+,	0.325 (1.7%)	1.12 0.51	45.5 3.0			
30^{Zn}	Zn^{68} (18.6) Zu^{68} (18.6)	0.1 1.0	Zn^{69m} Zn^{69}	14 hrs 52 min	β^-, β^-	0.92 0.9	0.44 none	95.5 —	66.6	$5.3 \cdot 10^4$ $1.97 \cdot 10^6$	10.8780 14.4986
Gallium	Ga^{69} (60.2)	1.4	Ga^{70}	20 min	β^-,	1.6	1.036 0.174	0.8 0.5	0.1	$1.2 \cdot 10^5$	11.6962
71^{Ga}	Ga^{71} (39.8)	3.4	Ga^{72}	14 hrs	β^-,	3.15 (9%) 2.5 (8%), 1.5 0.9; 0.6	0.84 2.2 0.63	96.7 21.4		$1 \cdot 10^3$	8.5172
Germanium 32^{Ge}	Ge^{70} (20.4) Ge^{74} (36.6) Ge^{76} (7.8)	3.0 0.45 0.2	Ge^{71} Ge^{75} Ge^{77}	11 days 82 min 12 hrs	 β^- β^-	1.137 (89%) 0.614 (15%) 2.196 1.379 0.71	 none 0.6 0.3	 —	0.1	$2.6 \cdot 10^3$ $2 \cdot 10^3$ $5.4 \cdot 10$	7.8633 7.6009 3.9890
Cadmium	Cd^{106} (1.22)	1.0	Cd^{107}	6,7 hrs	e^3,	0.32	0.864 0.510 0.094	0.5 0.62 9.50	0.1		
48^{Cd}	Cd^{110} (12.4)	0.2	Cd^{111m}	49 min	IP	—	0.15	25.0		$2.2.10^2$	5.3937
Indium	In^{113} (4.2)	56	In^{114m}	50 days	IP	—	0.772 0.556 0.192 1.3	3.5 3.5 18.5 0.09			
	In^{113} (4.2)	2.0	In^{114}	72 sec	β^-, e^3	~2.0	0.51 1.487	0.008 21.0	0.1		
49^{In}	In^{115} (95.8)	145	In^{116m}	54 min	β^-,	1.0 (51%) 0.87 (28%) 0.6 (21%)	1.274 1.085 0.406	75.0 54.0 25.0		$1 \cdot 10^6$	13.8155
	In^{115} (95.8)	52	In^{116}	13 sec	β^-	~3.0	none	—			

where $n\nu$ is the neutron flow in neutrons/cm^2/sec; σ is the cross section of the neutron activity of the elements, barns; N is the nuclear charge of the activated element; t is the irradiation time; and T is the half-life period.

It follows from the curves obtained that the indium-116 isotope has the best characteristic for its determination (activation cross section 145 b, half-life period 54 minutes). It should be noted that zinc-69 (with a half-life period 52 minutes) is the main interfering element in indium determination, but it gives a pure β-radiation which, in our setup, was completely absorbed in the aluminum filter fitted between the crystal and the sample. Analysis of the curves given in Fig. 3 gives the possibility of choosing a time interval of 5 minutes between the end of irradiation and the start of measurement. In order to standardize the apparatus, the curves

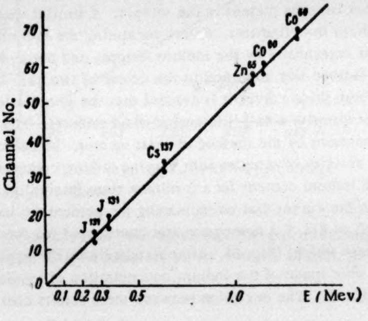

Fig. 2. The curve for the relation between the energy of the γ-quanta and the channel number.

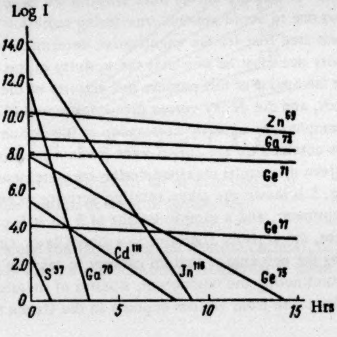

Fig. 3. Calculated curves for the drop in activity of the elements present in sphalerite.

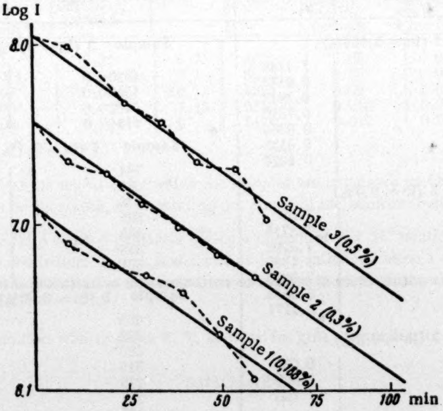

Fig. 4. Curves for drop in activity of a sample with various percentage contents of indium-116.

relating the activity of the sample and the percentage indium content of the sphalerite were constructed by means of standard samples very similar in chemical composition to natural sphalerite. Standard samples of sphalerite (ZnS) were irradiated for 3 hours 35 minutes (each) with slow neutrons from a polonium-beryllium source with an activity of 35 C. During this period it is indium-115 alone which is activated in practice.

The γ-radiation spectrum of the samples was measured by means of a scintillation γ-spectrometer. The shape of the γ-radiation spectrum of the indium-116 isotope is shown in Fig. 1, together with an indication of the energies on the photopeaks. In contrast to the data given in [5], where identification of the radioactive isotopes was carried out on the basis of the half-life periods, we investigated the change in intensity of the photopeaks (on the energy spectrum) with time; in our case the isotope was identified both by means of the characteristic lines of the spectrum (where there are no interfering lines of other isotopes), and by means of the half-life period. The decay curves were constructed on the basis of the change in the intensity of the photopeaks which allows one to avoid possible interfering radiation from other isotopes present in the sample. A similar method [6] was used first for the quantitative determination of indium in cylindrites. Before measuring the indium activity one must be sure that the activity of the sample is determined by the indium isotope, and not by some other isotope. For this purpose the activity of the indium isotope was measured in the course of two half-life periods, and the decay curves then constructed (Fig. 4). From these curves it is evident that the γ-radiation of the sample does actually correspond to the indium-116 isotope with a half-life period of 54 minutes. The points obtained on the curves were given a preliminary treatment by the method of least squares. In Table 2 are given the results obtained during measurements of the activity of samples with varying indium contents. In Fig. 5 is shown the curve relating activity to percentage indium content for a 5 minute time interval of measurement, and a sample weight of 5 g. It is clear from the curves that on increasing the percentage indium content, the activity conforms to a linear law. On the basis of Fig. 5 a nomogram was constructed for determining the percentage indium content in samples of different weight (Fig. 6). After standardizing the apparatus and constructing the nomogram, a series of measurements were made of the indium concentration of sphalerite samples taken from various deposits in the Uzbek SSR (Table 3). The deviation between these results does not

TABLE 2

Measurement of the Activity of Standard Samples

Activity N, cpm	Log N
Sample 1 (In = 0,168%)	
1231	7.1148
1010	6.9179
887	6.7879
838	6.7310
764	6.6386
610	6.4135
489	6.1924
Sample 2 (In = 0,3%)	
1906	7.580
1591	7.3715
1428	7.2998
1261	7.1389
1132	7.0300
950	6.8565
833	6.7171
Sample 3 (In = 0,5%)	
3090	0.035
2700	7.890
2150	7.750
Sample 3 (In = 0,5%)	
1820	7.610
1566	7.460
1477	7.320
1154	7.180
Sample 4 (In = 0,1%)	
781	6.6606
680	6.5221
578	6.3596
521	6.2384
430	6.0638
388	5.8610
321	5.7715
Sample 5 (In = 0,05%)	
495	6.2046
432	6.0685
380	5.9404
319	5.7653
275	5.6168
251	5.5255
205	5.3230

exceed 7% on an average, this is fully satisfactory for low (0.02%) indium concentrations. The errors which are caused by statistical measurement do not exceed ± 3%. The error introduced into the irradiation and measurement process (because of differences in the conditions of irradiation and measurement) lies within the limits ± 2-3% (for indium contents of the order of 0.1%). The effect of statistical errors can be decreased by increasing the counting rate, i.e., by increasing the weight of sample. Thus, when the sample weight is 50 g the statistical error does not exceed 1%.

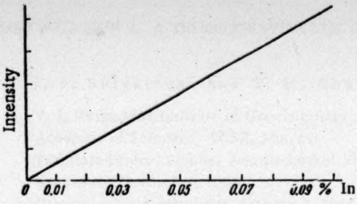

Fig. 5. Curve relating activity to percentage indium content.

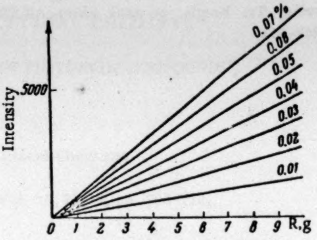

Fig. 6. Nomogram for determination of the indium content of sphalerites

What has been said shows that the given technique allows one (on increasing the neutron current) to determine fairly accurately small contents of indium in samples without radiochemical treatment of these samples.

TABLE 3

Determination of Indium by Chemical, Spectrographic, and Radioactivation Methods

Sample No.	Indium found, %		Deviation %	Sample No.	Indium found, %		Deviation %
	by chem. and spectrographic methods	by radioactivation method			by chem. and spectrographic methods	by radioactivation method	
7872	0.3	0.32	6.7	3601a	0.05	0.048	4.2
2247a	0.011	0.012	9.1	5620	0.07	0.068	10.4
281/п	0.02	0.022	10	4221	0.09	0.092	2.2
4760	0.03	0.028	7.15	3350	0.016	0.018	12.5
2724	0.02	0.021	5	5120	0.012	0.013	4.1

It should be noted that the duration for which the samples are irradiated can be decreased, and the sensitivity of the method can be increased, by increasing the power of the neutron source.

When a mark-space ratio neutron generator giving a current of 5×10^9 neutrons/4π sec is used, the duration of irradiation for the indium isotope is reduced to 10-15 minutes; when a suitable apparatus is available this should ensure an express quantitative determination of indium in rocks during core sampling by electrical means.

In conclusion, the authors wish to thank S. T. Badalov for gifts of samples for analysis.

SUMMARY

A method has been developed for the determination of the indium content of sphalerites; it is based on measurement of the γ-ray spectrum intensity of the activated samples by means of a scintillation γ-spectrometer. The concentration limits for the determination of indium in sphalerites is 0.1-0.01%. The probable experimental error is 5-10%. The method does not require radiochemical treatment of the samples.

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THE USE OF THERMOGRAVIMETRY IN ANALYTICAL CHEMISTRY

COMMUNICATION 2. A THERMOGRAVIMETRIC STUDY OF PLUTONIUM COMPOUNDS*

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The thermogravimetric method has been widely used by K. Duval [1, 2]. However, the thermobalances which he used were complicated and, accordingly, several authors have developed balances of simpler design [3-6]. The thermobalance which we have made was described in detail in [6]. Recently, an air damper has replaced the additional magnetic damper. The magnetic damper used originally required special calibration because of nonlinear readings on the ends of the scale.

The air damper consists of two assemblies of aluminum cylinders arranged concentrically at a distance of 5 mm from each other. A thermogravimetric study of a number of plutonium compounds was carried out on such a thermobalance.

Papers devoted to the thermogravimetric study of plutonium compounds have appeared recently [7, 8]. One of these papers [7], however, does not give any concrete experimental data, while in the other [8], only one compound – plutonium sulfate – was studied.

In our first communication [6] the thermogravigrams shown were expressed within the coordinates: change in weight (in scale divisions) – temperature. In the work described here, all the curves are presented within the coordinates: changes in weight of an aliquot (in %) – temperature. This facilitates establishment of the composition of intermediate compounds during a thermal decomposition.

According to B. Cunningham [9] pure crystalline plutonium dioxide contains 88.19% Pu. We have determined the percentage content of plutonium in the dioxide obtained from an accurately weighed aliquot of pure plutonium metal dissolved in 6 N HCl. The hydroxide was precipitated from solution by means of ammonia free from ammonium carbonate. The hydroxide was calcined at 1050°. Taking into account the negligible loss in the filtrate, the weight of dioxide obtained corresponded to a content of 88.23% of plutonium. We used this value in our subsequent calculations.

Since, from the point of view of gravimetric analysis, the most interesting parts of a thermogravigram are those parts on which no change in weight occurs with temperature changes, i.e., the areas corresponding to stable gravimetric forms, the first step is to characterize the temperature range which corresponds to such a plateau. We are of the opinion that one can only speak of a stable compound when its weight remains constant over a range of approximately 20°. In order to confirm the existence of a plateau it is necessary to carry out a repeated thermogravimetric study of the compound prepared, in this case, however, during the time that this horizontal part of the thermogravigram is being studied (not less than one hour) the temperature should be controlled thermostatically. When, under such conditions, the weight of the residue remains constant, it can be assumed that a stable compound is formed.

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* For Communication 1, see [6].

During a thermogravimetric study the temperature changes over a very wide range (20-1200°). Over this range the temperature can only be recorded by means of a Pt/Pt – Rh thermocouple, which, as is known, is calibrated with an accuracy of 1°. In our experiments the temperature was recorded visually on a pyrometer with a whole scale division of 20°. The accuracy with which the temperature was determined was about 5°.

We have studied the following plutonium compounds: the sulfate, iodate, oxalate, and 8-hydroxyquinolate.

Plutonium Sulfate. Some authors [8, 9] recommend anhydrous plutonium sulfate as a gravimetric form, since this compound has a more favorable conversion factor than plutonium dioxide, requires a low calcining temperature, and is readily dissolved after calcination. We have examined both plutonium sulfate tetrahydrate and anhydrous plutonium sulfate.

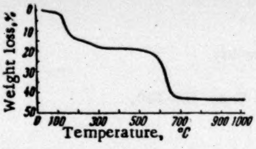

Fig. 1

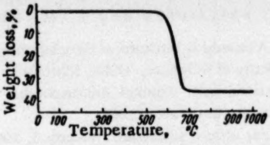

Fig. 2

The hydrated sulfate was precipitated by Anderson's method [10], by adding methanol to sulfuric acid solutions of plutonium. In Fig. 1 is shown a thermogravigram for hydrated plutonium sulfate. It is clear from this thermogravigram that all four water molecules have been lost by 270-280°. In the range 280 to 450° the curve has a plateau which corresponds to the anhydrous sulfate $Pu(SO_4)_2$. Above 450° the sulfate decomposes, decomposition is complete at 800° with formation of the dioxide.

Anhydrous plutonium sulfate was prepared by a method described by Drummond and Welch [8] (evaporation to dryness with H_2SO_4). A thermogravigram for anhydrous plutonium sulfate is shown in Fig. 2. It is clear from this that the sulfate is stable up to 500°.

Plutonium Iodate. There is no information at all in the literature [9, 11] as to the possibility of using plutonium iodate as a gravimetric form. Plutonium iodate was prepared by a technique which had been developed for precipitation of thorium iodate [12]. The precipitate obtained, after standing for two hours, was filtered off and washed with 0.05 N HNO_3 and with alcohol. The thermogravigram for plutonium iodate is shown in Fig. 3, three drops in the curve are clearly visible; the first corresponds to the removal of adsorbed water from the precipitate, this process is complete at 150°. The area on the curve covering the range 200-250° corresponds to the anhydrous iodate $Pu(IO_3)_4$.

The second drop on the curve corresponds to partial removal of oxygen with formation of an intermediate compound which is stable from 350-450°. A further increase in temperature above 450° leads to rapid decomposition of this compound to give plutonium dioxide.

Plutonium Oxalate. The oxalate of quadrivalent plutonium is one of the least soluble salts of plutonium. This oxalate is known to be precipitated with six molecules of water. There is, however, no definite information on the possibility of using this compound as a gravimetric form.

Plutonium oxalate hexahydrate was precipitated from nitric acid solutions by a method described by Cunningham [9]. In order to ensure complete precipitation, the yellow-green precipitate was allowed to stand overnight. It was washed with a 2% aqueous solution of oxalic acid and was dried under suction for one hour. The thermogravigram for the hexahydrate of plutonium oxalate is shown in Fig. 4. As is evident from this diagram, plutonium oxalate loses its six molecules of water within the range 30 to 110°. The short horizontal section on the curve at 120-150° corresponds to anhydrous plutonium oxalate. A further decrease in weight is connected with decomposition of plutonium oxalate to form plutonium dioxide. This process occurs in two stages. Initially plutonium carbonate is formed, at a temperature of 250° the carbonate starts to change into the dioxide. Accordingly, on the thermogravigram, at a temperature of 250°, we have a sharp break corresponding to this change. The sequence in which the oxalate decomposes can be represented by the following equations:

$$\mathrm{Pu}\,|\,\mathrm{C_2O_4}\,|_2\cdot 6\mathrm{H_2O} \rightarrow \mathrm{Pu}\,|\,\mathrm{C_2O_4}\,|_2 + 6\mathrm{H_2O}$$

$$\mathrm{Pu}\,|\,\mathrm{C_2O_4}\,|_2 \rightarrow \mathrm{Pu}\,|\,\mathrm{CO_3}\,|_2 + 2\mathrm{CO}$$

$$\mathrm{Pu}\,|\,\mathrm{CO_3}\,|_2 \rightarrow \mathrm{PuO_2} + 2\mathrm{CO_2}$$

Plutonium 8-Hydroxyquinolate. The number of organic derivatives of plutonium used in gravimetric analysis is small [14]. Its 8-hydroxyquinolate has been used by some authors for isolating plutonium from various solutions.

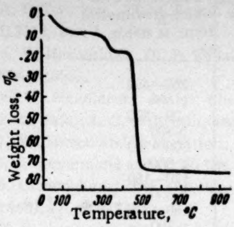

Fig. 3.

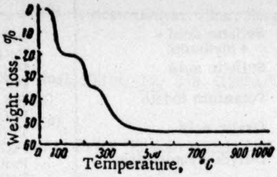

Fig. 4

The 8-hydroxyquinolate of quadrivalent plutonium was prepared as follows. To 10-15 ml of a nitric acid solution of a plutonium (IV) salt (3 mg Pu/ml and 1 N $\mathrm{HNO_3}$) was added 10-15 ml of a 10% solution of ammonium tartrate, 5 ml of water saturated with $\mathrm{SO_2}$, a few drops of 20% ammonia solution, and, after mixing, the solution obtained was heated to 50-70°. Next was added 20 ml of a 10% $\mathrm{NaHCO_3}$ solution heated to 50-70°. The plutonium was precipitated by dropwise addition of a 3% solution of 8-hydroxyquinoline (excess reagent 0.5-1 mg/ml). The red-brick crystalline precipitate which separated out was kept for 2 hours on a water bath. The filtered precipitate was washed with hot wash liquor (1% with respect to $\mathrm{NaHCO_3}$ and 0.05% with respect to 8-hydroxyquinoline) and then with hot water, a few drops of ammonia being added until the filtrate was completely clear. The precipitate was dried on the filter under suction for one hour.

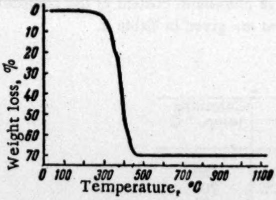

Fig. 5

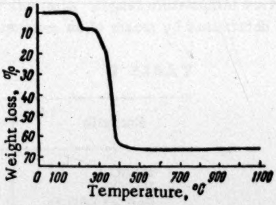

Fig. 6

In Fig. 5 is shown the curve illustrating the thermal decomposition of plutonium-8-hydroxyquinolate. Analysis of this curve shows that the 8-hydroxyquinolate is stable up to 220° and that it has the formula $\mathrm{Pu(C_9H_6NO)_4}$. Decomposition of this compound occurs at 300-500° with formation of plutonium dioxide. When the precipitate has not been washed free enough from precipitant, the thermogravigram (Fig. 6), at a temperature of about 200° shows an additional drop corresponding to removal of excess 8-hydroxyquinoline. Calculation shows that the small plateau on the thermogravimetric curve at 250° corresponds to the normal 8-hydroxyquinolate $\mathrm{Pu(C_9H_6NO)_4}$. Although 8-hydroxyquinoline itself starts to sublime at 85° [13], removal of excess of the reagent from the precipitate proceeds at a considerably higher temperature (about 200°), this indicates that there is a link between the molecule of precipitant and the precipitate of plutonium 8-hydroxyquinolate.

DISCUSSION OF RESULTS

Of the compounds which we have examined the ones which have the most favorable conversion factors are the iodate and 8-hydroxyquinolate of plutonium (Table 1). These compounds do not require a high calcining temperature.

TABLE 1

Precipitant	Gravimetric form	Conversion factor to Pu	Temp. range over which gravimetric form is stable, °C
Sulfuric acid + + methanol	$Pu(SO_4)_2$	0.554	280—450
	PuO_2	0.882	>800
Sulfuric acid	$Pu(SO_4)_2$	0.554	20—500
	PuO_2	0.882	>800
Potassium iodate	$Pu(JO_3)_4$	0.254	200—250
	PuO_2	0.882	≥ 800
Oxalic acid	$Pu(C_2O_4)_2$	0.576	120—150
	PuO_2	0.882	>600
8-Hydroxyquinoline	$Pu(C_9H_6NO)_4$	0.293	50—230
	PaO_2	0.882	>700

Plutonium sulfate — a compound with a fairly favorable conversion factor (0.554) and a large temperature range over which it is stable — is little used in gravimetric analysis. Plutonium sulfate recommends itself as a gravimetric form because the residue of plutonium sulfate obtained after calcining up to 450° is readily brought into solution.

Decomposition of plutonium compounds to give the dioxide finishes at higher temperatures in those cases where it is formed from inorganic compounds than in cases where it is formed from organic compounds.

The results obtained make it possible to establish more favorable temperatures for drying and calcining the compounds studied.

We have carried out special experiments to confirm the formation of compounds of a definite composition within the given temperature ranges. After calcination, the percentage plutonium content of the compounds isolated was determined by means of an α-count. The results obtained are given in Table 2.

TABLE 2

Formula	Pu content, %		Calcining temp. °C
	calc.	found	
$Pu(SO_4)_2$	55.45	55.70—55.31	450
$Pu(JO_3)_4$	25.45	25.30—25.26	200
$Pu(C_2O_4)_2 6H_2O$	45.69	45.50	20
$Pu(C_2O_4)_2$	57.59	57.10	140
$Pu(C_9H_6NO)_4$	29.3	28.71—29.46	230

As is evident from the results given in this table, we obtained values close to the theoretical values.

SUMMARY

It has been shown that $Pu(SO_4)_2$ obtained from both plutonium sulfate tetrahydrate and the anhydrous sulfate can be used as a gravimetric form.

When plutonium iodate is used in gravimetric analysis, it is essential to wash it free from excess precipitant, the precipitate can then be dried at 200°.

It has been shown that the anhydrous oxalate of quadrivalent plutonium can be used for gravimetric determinations. For this purpose, plutonium oxalate hexahydrate should be dried at 140-150°.

Plutonium 8-hydroxyquinolate, after drying at 230° (not above 250°) corresponds to the formula $Pu(C_9H_6NO)_4$ and can be used as a gravimetric form.

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QUANTITATIVE SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN THE RARE EARTHS

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The sensitivity of x-ray spectrographic determination of impurities in the rare earths, which is equal to 0.1%, is already insufficient for controlling modern production of preparations of the rare earths.

Encouraging results are given by emission spectrographic methods of analysis, such methods enable one, with small expenditure of test material, to attain a high sensitivity which amounts to 0.02-0.005% for yttrium group elements.

Improvement in methods of emission spectrographic determination of the rare earths has taken place very slowly [1-24], as a consequence of the complexity of their spectra and the nonavailability of spectrographically pure preparations which are essential for identification of lines and for preparation of standards.

The most important and most systematic work along this direction has been carried out by Fassel and coworkers [5, 11, 12, 16, 17].

Fassel's method is based on complete ignition of the sample, which is in the form of a mixture of the test element and carbon powder, the main element of the sample being suggested as the internal standard. In order to carry out an analysis by Fassel's method about 15 mg of sample is necessary. Developing the work of Fassel, Grishina recently [18, 19] suggested a method for the determination of a number of impurities in pure preparations of the rare earths, in which solutions of the chlorides placed on the face of a carbon or copper electrode are used. The method is characterized by high sensitivity (0.02-0.05%) and only uses up a very small amount of material (2-4 mg). The experimental error is 5-10%.

The problem which we set ourselves was to determine the range of elements which may be present as impurities in various preparations during their purification. For this purpose, we subjected to qualitative, and, subsequently, to semiquantitative spectrographic analysis, a number of rare earth preparations, the impurity content of which was less than the sensitivity of determination by x-ray spectrographic methods.

The distribution of impurity elements in various rare earth preparations, after their purification by chromatographic methods, is shown in Table 1.

As is evident from the table, the purified rare earth preparations contain as impurities mainly the neighboring elements in the periodic system. Development of methods for the determination of these neighboring elements should take precedence.

We have developed the following analytical method for the quantitative determination of small amounts of impurities, this method does not require the use of pure preparations for preparing standards. In essence, the method depends on using the relationship between the line intensity and the absolute content of the test element in the sample being analyzed. One standard, which is one of the samples carefully analyzed by an x-ray spectrographic method, is used for carrying out an analysis.

The content of rare earth impurities in this sample should be higher than the sensitivity limit of the x-ray spectrographic methods of analysis (> 0.1%) and should lie within the range 0.5-1%.

TABLE 1

Distribution of Impurity Elements in Some Rare Earth Preparations

Test element	Impurity element content, %
Pr	Eu ~ 0.01
Nd	Pr ~ 0.1
Sm	Eu ~ 0.1
Eu	Sm ~ 0.5; Gd ~ 0.02
Gd	Tb ~ 0.02
Tb	Dy ~ 0.02; Gd ~ 0.04; Y ~ 0.01
Y	Yb ~ 0.007; Ho ~ 0.02; Dy ~ 0.04; Tb ~ 0.04; Gd ~ 0,02
Dy	Y ~ 0.04; Ho ~ 0.03; Tb ~ 0.02
Ho	Dy ~ 0.02
Er	Yb ~ 0.006
Tu	Yb ~ 0.006
Lu	Yb ~ 0.02; Tu ~ 0.02

In order to determine impurities, the content of which is less than 0.1%, a curve showing the relation log I = f (log m) – where I is the line intensity, m is the absolute content of the element, and is proportional to the weight of sample taken – is constructed on the basis of this standard. By decreasing the amount of sample, it is possible to follow the path of the calibration curve right down to very low values of the absolute content, which are limited by the absolute sensitivity of the spectrographic determination of the elements. In order to establish the path of the calibration curve more reliably in regions of low m and high m, several standards[*] are used.

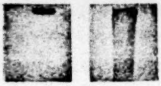

Fig. 1. Radiograph of the distribution of La-140 in the body of a carbon electrode after placing ten drops of a 5% solution of the La-140 isotope in 1% hydrochloric acid on its face. On the right: without treatment of the electrode face with polystyrene; on the left: the electrode was treated with polystyrene before putting the lanthanum isotope on it.

Bearing in mind the necessity for cutting down the amount of material expended, we used a solution of the chlorides of the rare earths in order to develop the method, the solutions being placed on the face of the electrode, since under such conditions, the amount of material expended is a minimum.

Standards and test samples are dissolved as follows.

Rare earth oxides are dissolved in concentrated hydrochloric acid on heating. The solutions are evaporated to dryness, and from the chlorides obtained, 5% solutions of the rare earths in 1% hydrochloric acid are prepared. One drop of this solution is placed on the face of a carbon or copper electrode, the latter being then dried on a hot plate. 5%, 3%, 1%, 0.3%, etc. solutions of the main standard are used as standards.

In the spectral regions 3100-3500 A, 4200-4600 A carbon electrodes are used, while in the region 3750-4200 A copper electrodes are used. An ac arc is used for spectra excitation.

A special study was made of the treatment of the electrodes prior to placing samples on them. For this purpose, radioactive preparations of the rare earths were placed on the faces of the electrodes, the electrodes were then examined radiographically. It was established that the rare earths are distributed fairly evenly on the electrode face, but diffusion into the body of the electrode occurs (Fig. 1), and this leads to some drop in sensitivity. In order to eliminate this diffusion, the carbon electrode was covered beforehand with a polystyrene film, the latter being formed by drying out a 3% solution of polystyrene in benzene on the face. This polystyrene treatment ensures that the rare earths are concentrated on the electrode surface only (Fig. 1).

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[*] Naturally, in the m region the analytical lines should be free from self-absorption.

The spectra were taken by means of a Baird Associates diffraction spectrograph which had a dispersion of 5.5 A/mm in the first order. Two electrodes plus samples were exposed on the same place on the photographic plate. The analytical conditions are given below.

Spectrograph	Baird Associates with a diffraction grating, second order, dispersion 2.75 A/mm.
Slit width	25 μ.
Illumination	Single lens system.
Electrodes	Copper or carbon with a diameter of 6 mm. The upper electrode was sharpened to a cone.
Excitation source	ac arc generator.
Current	10 a for carbon electrodes and 8 a for copper electrodes.
Exposure	60 sec. Two electrodes plus samples were exposed on the same place for 30 sec. each.
Plates	Spectrographic, type II, sensitivity 16 or 22 GOST units.
Developer	Meto-hydroquinone
Calibration of emulsion	Sector or stepwise attenuator

TABLE 2

Analytical Lines for the Determination of Impurities in the Rare Earths

Impurity	Base	Wavelength of the lines, A analytical lines	 reference line for analysis by three standards method	Conc. range, %	Electrodes
La	Pr	3337.49	3337.19	0.005—0.2	Carbon
Sm	Nd	4433.88	4436.68	0.05 —0.2	•
Eu	Nd	4435.53	4436.68	0.01 —0.1	•
Pr	Nd	4408.84	4419.62	0.1 —1.0	•
Sm	Eu	4424.34	4357.04	0.05 —1.0	•
Yb	Eu	3289.85	3288.57	0.008—0.5	•
Eu	Gd	4435.53	4437.45	0.02 —0.2	•
Tb	Gd	3324.40	3321.7	0.01 —0.2	•
Dy	Tb	3898.54	3893.73	0.02 —0.2	•
Gd	Tb	3350.48	3347.8	0.02 —0.2	•
Gd	Tb	3768.41	3761.9	0.02 —0.2	Copper
Y	Tb	3982.59	3986.97	0.02 —0.2	Carbon
Y	Tb	3774.33	3761.9	0.02 —0.2	Copper
Y	Dy	3774.33	3777.9	0.008—0.2	•
Er	Ho	3906.32	3910.3	0.02 —0.1	•
Dy	Ho	4211.72	4219.2	0.02 —0.2	•
Ho	Er	4103.84	4104.02	0.02 —0.2	•
Tu	Er	3362.61	3369.23	0.008—0.2	Carbon
Tu	Yb	3362.61	—	0.003—0.2	•
Dy	Y	3407.80	3469.43	0.01 —0.2	•
Tb	Y	3218.93	3182.42	0.02 —0.2	•
Yb	Tu	3289.37	3291.00	0.008—0.2	•
Yb	Lu	3289.37	3171.36	0.003—0.2	•
Tu	Lu	3362.61	—	0.008—0.2	•

Table 2 contains the recommended analytical lines. These lines were chosen on the basis of the spectra of decreasing amounts of samples. Identification and checking of the lines for absence of superposition was carried out by controlling the change in the line intensity during the purification of the preparations.

In order to decipher and distinguish spectra of different orders we used a color photography method suggested earlier [20]; this is based on the fact that lines of different orders have different colors. This makes it possible to remove foreign lines readily by means of their color, and to isolate false "ghost" lines.

Calibration curves are constructed within the coordinates log I, log m; in the region of normal blackening, within the coordinates S, log m; where m is the absolute content of the elements determined. In Fig. 2, as an example, is shown one of the calibration curves obtained.

The mean square error for a single determination by the method indicated is 25-30%.

Bearing in mind the close physicochemical properties of the rare earths, one might expect that the calibration curves constructed for the determination of impurities in some rare earth preparation might coincide with the calibration curves* for the determination of the same impurities in other rare earth preparations.

Experiments, which we carried out on materials based on erbium and yttrium, showed that, in actual fact, coincidence of the calibration curves does occur for the elements indicated (Fig. 3). It can be assumed that coincidence of calibration curves will also take place for other rare earths.

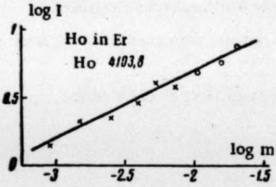

Fig. 2. Calibration curve for the determination of holmium in erbium by the method of diluting the standard. o) Basic standards analyzed by x-ray spectrographic analysis; x) standards obtained by diluting the basic standard.

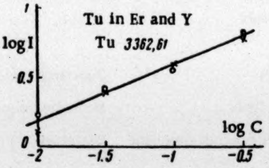

Fig. 3. Calibration curve for the determination of thullium in erbium and yttrium. o) Points belonging to erbium; x) points belonging to yttrium.

In order to check on the absence of systematic errors during determinations by the methods described above, we also used the three standards method.

Standards were prepared by the usual methods from the purified preparations. Calibration curves were constructed within the coordinates ΔS, log C or log $\frac{I_{line}}{I_{mean}}$, log C. The recommended analytical lines and the reference lines used in this method are also given in Table 2. The analytical conditions were the same as those described above.

TABLE 3

Comparison of the Results Obtained During the Determination of Thullium and Holmium in Erbium by Various Methods

Introduced, %	Found by the method of diluting a standard, %	Found graphically on a yttrium base, %	Found graphically on an erbium base, %
Tu in Er 0.03	0.02	0.035	0.033
Error	33%	16.7%	10%
Ho in Er 0.04	0.03	0.045	0.043
Error	25%	12.5%	7.5%

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* Within the coordinates S, log C or log I, log C.

The mean square error of a single determination by the three standards method is 10-15%.

Table 3 contains results obtained during the determination of Tu and Ho in Er.

As is evident from the table, the analytical results coincide within the limits of experimental error.

The authors wish to thank E. E. Vainshtein for his help and valuable advice during the course of this work.

SUMMARY

A method has been developed for the quantitative spectrographic determination of small amounts of impurities of La in Pr; Sm, Pr, and Eu in Nd; Sm and Yb in Eu; Eu and Tb in Gd; Y, Dy, and Gd in Tb; Y in Dy; Er and Dy in Ho; Ho and Tu in Er; Tu in Yb; Dy in Y; Tb in Y; Yb and Tu in Lu; and Yb in Tu.

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A CHEMICOSPECTROGRAPHIC METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF MOLYBDENUM AND TUNGSTEN IN THE PRESENCE OF LARGE AMOUNTS OF IRON

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Spectrographic determination of small amounts of molybdenum and tungsten in ores and meteorites containing more than 15% of iron is connected with considerably difficulties, and, in the presence of more than 90% of iron, such a determination becomes impossible. In order to carry out an analysis under these conditions it is necessary to separate the test elements quantitatively from iron beforehand. In the work described here we used ion exchange chromatography for this purpose.

Ion exchange chromatography has been used for separating molybdenum from other metals, including iron [1-6]. Chromatographic separation of tungsten has been studied in less detail, while the possibility of using this method for the simultaneous separation of Mo and W from rocks, has not been examined hitherto, as far as we know.

One of the methods for separating Mo and Fe is based on making use of the property of molybdenum to form a peracid with H_2O_2, this compound is not held back on a cation exchange resin and passes through into the filtrate, while iron is held on the resin [1]. The possibility of separating molybdenum from accompanying elements in the form of its citrate complex has been noted [2, 6]. In order to choose the optimum conditions for carrying out chromatographic experiments and to establish the possibility of simultaneously separating the elements from rocks, the radioactive isotopes Mo^{99} and W^{185} were used.

Experiments were carried out on a column 10-12 mm in diameter containing 10-12 g of the cation exchange resin KU-2. The solution was passed through the column at the rate of 2-3 ml/min. The optimum acidity and the volume of wash liquors, and the H_2O_2 concentration or that of the complexing agent used for separating Mo and W from iron, were established using solutions containing 120 mg of Fe in the form of ferric alum, and 0.1 mg of Mo or W in the form of ammonium molybdate or tungstate. The latter contained the radioactive isotopes, the radiation intensity of these isotopes in the filtrate was recorded on the basis of their β-activity by means of a torsion counter. The acidity of the solution was altered by addition of the calculated amount of sulfuric acid. The curves (Figs. 1-4) illustrate the relation between the percentage yield of Mo and W in the filtrate and the acidity of the solution and the H_2O_2 concentration in the first of the methods tested, and acidity and citric acid concentration in the second of the methods tested.

Alternate portions of filtrate were chosen and analyzed every 3 minutes. The wash solution was prepared by dissolving four drops of concentrated sulfuric acid in 100 ml of water. The minimum amount of wash liquor required for complete elution of Mo and W from the columns proved to be 150-180 ml.

Examination of the curves (Figs. 1-4) shows that the method suggested by Alimarin and Medvedeva [1] for the chromatographic separation of molybdenum from iron can also be successfully used for the quantitative simultaneous separation of tungsten. The optimum conditions for this purpose are obtained at a H_2O_2 concentration of 1% and an acidity of 0.5 N with respect to H_2SO_4. As special checks using labelled atoms showed, under the conditions indicated, Mo and W are not held by the cation exchange resin, and pass almost completely into the filtrate. During separation of these elements in the form of their citrate complexes (Figs. 3 and 4) we were unable to obtain complete separation of tungsten, only about 75% of the original amount of this element originally present in the rock passed into the filtrate.

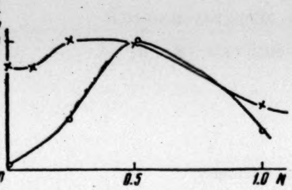

Fig. 1. The relation between the yield of W (○) and Mo (x) in the filtrate and the acidity of the solution during their chromatographic separation from iron by method [1]; the amount of labelled Mo or W atoms as a percentage of the total amount isolated is plotted on the ordinate, while the acidity expressed in g-eq H_2SO_4/liter is plotted along the abscissa.

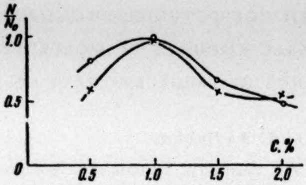

Fig. 2. Relation between sorption of W (○) and Mo (x) by the cation exchange resin and the H_2O_2 concentration expressed as a percentage.

Experimental Procedure. Having established the possibility of separating Mo and W quantitatively by a chromatographic method, from large amounts of iron, which interfere with their determination, we were able to develop a combined chemicospectrographic method for the determination of these elements in rocks, and we have successfully used this method for the analysis of meteorites. For this purpose 0.12 g of test material is heated with 15 ml of HCl (1 : 1), 0.5 ml of concentrated HNO_3 is added and the mixture heated again until the material has dissolved completely; the solution is then evaporated until its volume is 3-5 ml and 10-15 ml of 6 N H_2SO_4 is added, the solution is evaporated until thick fumes of SO_3 cease to be evolved. To the dry residue is added 30 ml of water and the whole heated until complete solution is obtained. The solution is cooled and sulfuric acid added until the concentration of the solution is 0.45 N with respect to H_2SO_4 (this corresponds to a pH of 0.65), H_2O_2 is added until its concentration in the solution is 1%. The solution thus prepared is passed through a column containing KU-2 at the rate of 3 ml/min, the column is washed with 180 ml of wash liquor and all the filtrate collected and evaporated to dryness. The residue obtained is calcined to constant weight (about 2 mg); it is then diluted to 20 mg with

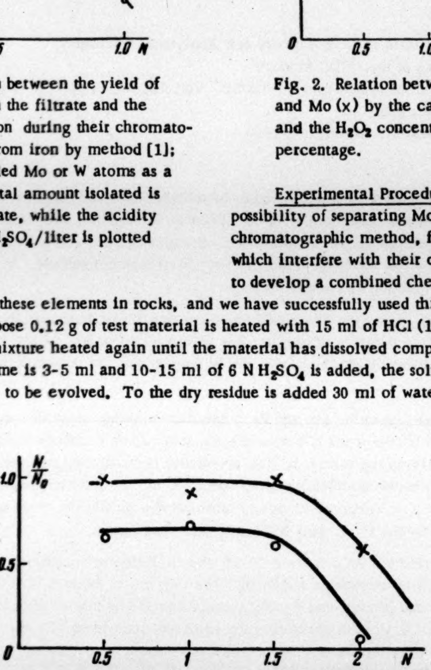

Fig. 3. The relation between yield of W (○) and Mo (x) in the filtrate, and the acidity of the solution, during their chromatographic separation from iron by method [2, 6].

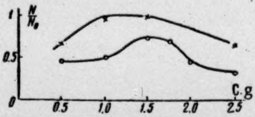

Fig. 4. Relation between yield of W (○) and Mo (x) in the filtrate and citric acid concentration expressed in g.

a silicate base which has been shown to be free from Mo and W, the mixture is divided into two portions in which Mo and W are determined spectrographically [7-9].

The reproducibility of the experimental results is ± 12 % for Mo and ± 15 % for W. The sensitivity of the chemicospectrographic method (taking into account the five-fold enrichment of the elements which occurs in our experiments during chemical preparation of the sample) is $2 \cdot 10^{-5}$ % for molybdenum and $6 \cdot 10^{-4}$ % for tungsten. This is quite satisfactory for the determination of the content of these elements in iron meteorites.

Some of the results which we obtained during such determinations are given in the table. Comparison of these results with published results [10, 11] indicates that there is good agreement between the experimental results which we obtained on using the method described and those obtained by other workers using a spectrophotometric method.

Mo and W Contents of Some Meteorites

Metallic phase of the iron meteorite	Found, %	
	Mo	W
Meteorite "Sikhote-Alinskii"	$1.68 \cdot 10^{-3}$	$9.5 \cdot 10^{-4}$
Meteorite "Toluka"	$1.5 \cdot 10^{-3}$	$9.2 \cdot 10^{-4}$
Meteorite "Saratov"	$8.1 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$
Meteorite "Kunashak"	$8 \cdot 10^{-4}$	$5.7 \cdot 10^{-4}$

The author wishes to express his thanks to E. E. Vainshtein for his valuable advice, and to L. V. Meshcheryakova for help in carrying out the analyses.

SUMMARY

During the spectrographic determination of Mo and W in meteorites containing large amounts of iron, these elements are separated from the iron chromatographically.

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THE USE OF CINNAMIC ACID IN ANALYTICAL CHEMISTRY

COMMUNICATION 1. SEPARATION OF IRON, ALUMINUM, AND CHROMIUM FROM MANGANESE, NICKEL, COBALT, AND ZINC

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Methods of separating trivalent metals from divalent metals in the form of basic acetates, succinates, or formates have not found wide application. Somewhat better results have been obtained by using ammonium benzoate [1], which precipitates the basic benzoates of trivalent and quadrivalent metals at a definite pH of the solution. The basic benzoates of iron, aluminum, and chromium, however, which do not possess a constant composition and separate out in a strongly hydrated form, are capable, after they have separated out, of partially coprecipitating the divalent metals remaining in the solution (Mn, Ni, Co, and Zn), the extent of coprecipitation being dependent on the excess of precipitant added.

In order to improve the method of separating the metals indicated by hydrolysis, we decided to examine the possibility of using other acids of the aromatic series for this purpose, in the first instance we tried cinnamic acid (phenyl acrylic acid). During separation of the metals, cinnamic acid has been used for: precipitating vanadium [2]; for separating thorium from the rare earths [3]; and for precipitating zirconium [4]; for separating thorium from uranium [5]; and for separating thorium from the rare earths and from other metals [6].

Solutions of the metal chlorides were prepared for the study; the solutions were standardized gravimetrically. Our experiments showed that, under certain conditions, ammonium cinnamate quantitatively precipitates iron, aluminum, and chromium in the form of their basic cinnamates from a weakly acid solution heated to the boiling point; under these conditions, manganese, nickel, cobalt, and zinc remain in solution. During these experiments the pH of the solution was kept at 5.0-5.1.

The pH value at which separation of the basic cinnamates of the indicated metals starts, almost coincides with the pH values at which their hydroxides separate from solution.

In order to establish their composition, the precipitates were filtered off through glass filters, washed 2-3 times with water containing ammonium cinnamate, and then with alcohol. After drying to constant weight at 110°, the precipitates were analyzed. We established that iron gives a mixture of basic salts $C_6H_5CH:CH\cdot COO\cdot Fe(OH)_2$ and $(C_6H_5CH:CH\cdot COO)_2Fe(OH)$ (in the proportion of about 1:1); aluminum and chromium gives basic salts $(C_6H_5CH:CH\cdot COO)_2Al(OH)$ and $(C_6H_5CH:CH\cdot COO)_2Cr(OH)$. On using double the amount of reagent for carrying out the precipitation, the composition of the basic salts of aluminum and chromium did not change; iron, however, gave a mixture of the medium and basic salts: $(C_6H_5CH:CH\cdot COO)_3Fe$ and $(C_6H_5CH:CH\cdot COO)_2Fe(OH)$ (in the proportion of about 1:1).

In order to study the quantitative separation of iron, aluminum, and chromium, precipitation experiments were carried out under the conditions described below. The experimental results are given in Table 1. The filtrates obtained after removal of iron, aluminum, and chromium were evaporated and tested for the presence of the metals indicated; they were not detected in a single case. Precipitation in the presence of $(NH_4)_2SO_4$ and NH_4NO_3 taken in amounts of 10 g also proceeded quantitatively. The precipitates of the basic cinnamates of iron, aluminum, and chromium coagulated readily and were easily filtered and washed.

TABLE 1

Oxide	Taken g	Found g	Error g	Oxide	Taken g	Found g	Error g
Fe_2O_3	0.0550	0.0549	−0.0001	Al_2O_3	0.0005	0.0005	±0.0000
Fe_2O_3	0.0006	0.0006	±0.0000	Cr_2O_3	0.0532	0.0532	±0.0000
Al_2O_3	0.512	0.0511	−0.0001	Cr_2O_3	0.0005	0.0006	+0.0001

Experiments which were carried out in order to study the extent to which the basic cinnamates of iron, aluminum, and chromium are contaminated by the divalent metals (Mn, Ni, Co, and Zn) were carried out under the same conditions. In order to determine the divalent metals entrained by the precipitates of the trivalent metals, the precipitates were ashed and then dissolved, and Mn, Ni, Co, and Zn were determined colorimetrically in the solutions. The extent of contamination is shown in Table 2. The experimental results show that separation is fairly complete, and that there is no need to carry out a reprecipitation.

TABLE 2

Taken, g				Found in the precipitate, g	
Fe_2O_3	0.0500	MnO	0.0050	MnO	<0.00001
	0.0050	MnO	0.0500	MnO	0.00008
	0.0500	NiO	0.0050	NiO	<0.00001
	0.0050	NiO	0.0500	NiO	0.00002
	0.0500	CoO	0.0050	CoO	0.00003
	0.0050	CoO	0.0500	CoO	0.00008
	0.0500	ZnO	0.0050	ZnO	0.00006
	0.0050	ZnO	0.0500	ZnO	0.00002
Al_2O_3	0.0500	MnO	0.0050	MnO	0.00001
	0.0050	MnO	0.0500	MnO	0.00002
	0.0500	NiO	0.0050	NiO	0.00007
	0.0050	NiO	0.0500	NiO	0.00006
	0.0500	CoO	0.0050	CoO	0.00007*
	0.0050	CoO	0.0500	CoO	0.00005*
	0.0500	ZnO	0.0050	ZnO	0.00006
	0.0050	ZnO	0.0500	ZnO	0.00003
Cr_2O_3	0.0500	MnO	0.0050	MnO	0.00003*
	0.0050	MnO	0.0500	MnO	0.00004*
	0.0500	NiO	0.0050	NiO	0.00003*
	0.0050	NiO	0.0500	NiO	0.00007
	0.0500	CoO	0.0050	CoO	0.00002*
	0.0050	CoO	0.0500	CoO	0.00008*
	0.0500	ZnO	0.0050	ZnO	0.00003*
	0.0050	ZnO	0.0500	ZnO	0.00005*

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* Precipitation carried out in the presence of 15 g NH_4Cl.

During separation of total trivalent metals from the divalent metals the extent of separation was also fully satisfactory.

After removal of iron, aluminum, and chromium in the form of their basic cinnamates, the divalent metals indicated were quantitatively precipitated from the filtrates by heating the latter with ammonium sulfide. Hydrogen sulfide quantitatively precipitates zinc, cobalt, and nickel, the precipitates of the last two metals separating out as crystalline sulfides, while zinc separates out in the form of an amorphous, fairly dense sulfide. Under these conditions, manganese does not separate out at all initially, only after some time does a slight turbidity appear. During separate determination of the divalent metals in the filtrates, manganese was precipitated in the form of manganese ammonium phosphate which was then calcined to the pyrophosphate. Nickel was isolated, as usual, by means of dimethylglyoxime from a weakly ammoniacal medium, and was left to stand overnight. Cobalt was isolated by means of α-nitroso-β-naphthol from a heated solution acidified with hydrochloric acid. The precipitate was carefully ashed to the oxide which was dissolved in HCl, after evaporating and neutralizing this solution, the cobalt was isolated as its anthranilate [7]. Zinc was isolated by means of an alcoholic solution of hydroxyquinoline from a heated, weakly ammoniacal solution, and, after the precipitate had been washed, it was calcined to zinc oxide. Completely satisfactory results were obtained (Table 3).

TABLE 3

Taken, g		Found, g	Error, g
Fe_2O_3 0.0100 Al_2O_3 0.0100 Cr_2O_3 0.0100	MnO 0.0107	MnO 0.0109	+0.0002
Fe_2O_3 0.0100 Al_2O_3 0.0100 Cr_2O_3 0.0100	NiO 0.0107	NiO 0.0107	±0.0000
Fe_2O_3 0.0100 Al_2O_3 0.0100 Cr_2O_3 0.0100	CoO 0.0104	CoO 0.0105	+0.0001
Fe_2O_3 0.0100 Al_2O_3 0.0100 Cr_2O_3 0.0100	ZnO 0.0104	ZnO 0.0105	+0.0001

Preparation of the Reagent. A solution of ammonium cinnamate (5% with respect to cinnamic acid) is used as the reagent. 25 g of pure cinnamic acid is placed in a 750-800 ml conical flask (having a mark at 500 ml) fitted with a glass stopper. Approximately 80 ml of water is added and the contents of the flask mixed to a homogeneous paste with a glass rod with a widened end, care being taken to break down any lumps. A further 200 ml of water is added and a 10-12% solution of distilled ammonia added in small portions with vigorous stirring, until the cinnamic acid has almost completely dissolved (a small amount of material should be left, while the liquid should not smell of ammonia). A small amount (about 1.5 g) of cinnamic acid is added and the whole thoroughly mixed after stoppering the flask. The solution should give a weak acid reaction to litmus. Water is added to bring the volume up to 500 ml and the whole thoroughly mixed again; the final solution is left to stand overnight and then filtered through a "blue band" filter. The reagent is stored in dark colored glass bottles fitted with glass stoppers. The reagent is stable, a small amount of a crystalline sediment of cinnamic acid separates out with time, but this does not interfere.

Experimental procedure. It is best to have a hydrochloric acid solution which does not contain more than 0.1 g of the sesquioxides (sulfates and nitrates do not interfere).

To about 60 ml of the acid solution is added 10 g of ammonium chloride. In those cases when the trivalent metals present are mainly aluminum or chromium, and the iron content is very low, the amount of NH_4Cl should be increased to 15 g. The solution is carefully neutralized with dilute ammonia, the latter being added dropwise with stirring until a faint turbidity appears, the latter is destroyed by addition of 2-3 drops of hydrochloric acid sp. gr. 1.12. When large amounts of iron are present, neutralization is carried out to the appearance of a brownish color, the latter too being destroyed by addition of the indicated amount of hydrochloric acid. The solution obtained is diluted with water to approximately 80-90 ml and then heated to the boil. Having adjusted the flame so as to maintain gentle boiling, 20 ml of the reagent is added dropwise from a dropping funnel with a bent tip, the solution being vigorously stirred at the same time with a glass rod.

On completion of the precipitation, the beaker is covered with a clock glass and the liquid allowed to boil weakly for 1-2 minutes (in the presence of large amounts of chromium, up to 3 minutes). The beaker is then transferred to a water bath for 1-1.5 hours. The liquid is stirred from time to time while it is on the water bath. After the precipitate has settled out, the liquid is filtered through a "white band" filter, during this stage the liquid is carefully decanted, while endeavouring not to disturb the mass of the precipitate. The precipitate remaining in the beaker is washed twice by decantation with hot wash liquor (10 g of NH_4Cl is dissolved in hot water, 20 ml of reagent is added, and the volume made up to 100 ml), using 20-25 lots of the latter. The precipitate is finally transferred onto the filter and washed with hot wash liquor (to 20 ml of reagent is added

280 ml of hot water). The washed precipitate is transferred to a crucible, in which it is carefully dried and ashed.

Manganese, nickel, cobalt, and zinc can be separated from the filtrate by means of ammonium sulfide on heating. Subsequently, zinc can be removed in the form of its sulfide [8], nickel and cobalt are separated from manganese by precipitating them in the form of their crystalline sulfides by means of hydrogen sulfide in the presence of a buffer mixture consisting of pyridine and its hydrochloride [9]. When only one of the divalent metals is present, it can be isolated and determined as indicated earlier.

The method can be used for the analysis of the most diverse materials such as manganese ores and concentrates, marine iron-manganese concretions, nickel, cobalt, and zinc ores, and various alloys.

SUMMARY

It has been established that ammonium cinnamate quantitatively precipitates iron, aluminum, and chromium in the form of their basic salt from a weakly acid solution on heating; under the same conditions, manganese, nickel, cobalt, and zinc remain in solution.

The basic cinnamates of iron, aluminum, and chromium are precipitated in a dense form which is readily filtered and washed. Sorption of the divalent metals (Mn, Ni, Co, and Zn) by the precipitates of the basic salts is so negligible, that separation can be effected after only one separation. Sulfate and nitrate ions do not interfere.

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A METHOD FOR THE INDIRECT POLAROGRAPHIC DETERMINATION OF SULFATE, AND ITS USE IN WATER ANALYSIS*

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In a paper published earlier [1] a study was made of the system $SO_4^{2-} - Pb^{2+}/PbSO_4$ for the purpose of developing a method for the indirect polarographic determination of sulfate. When a solution containing sulfate, and with a definite ionic strength and temperature, is shaken with lead sulfate, a state of equilibrium is established which can be characterized by the polarographic determination of the concentration of lead ions which pass into solution. A method of determining sulfate in water is based on this principle [2].

In the present article a description is given of another method for the indirect polarographic determination of sulfate, which is based on precipitation of sulfate ions from an aqueous-alcoholic medium by addition of lead nitrate, and polarographic determination of the lead ions remaining in solution. The presence of ethanol ensures more complete precipitation of lead sulfate. Since excess lead ions are determined in the final solution polarographically, precipitation is carried out in the presence of potassium nitrate which subsequently serves as the supporting electrolyte. The new method is simpler.

Apparatus. 1) A Leybold polarograph with a capillary from the same firm; 2) a Heyrovsky polarographic cell (the temperature is controlled within the limits of ± 0.5°); 3) an ion exchange column prepared according to Tompkins et al. [3].

Reagents. 1) Potassium sulfate solution 0.01 M. More dilute solutions were prepared from this solution; 2) potassium nitrate solutions 0.5 and 0.1 M; 3) ethanol; 4) gelatin solutions, 0.2 and 0.4%; 5) lead nitrate solutions, 0.01 and 0.004 M; 6) Amberlite IR-120 (in the H-form).

Preliminary Experiments. In order to establish the optimum conditions for the indirect polarographic determination of the concentration of lead ions in solution (in the absence of sulfate) a solution with a concentration of 10^{-3} M was taken, this concentration is the optimum for measuring the diffusion current of lead ions. The solubility of lead sulfate drops strongly in a medium containing 25% ethanol; higher ethanol concentrations lead to coprecipitation and decrease the height of the polarographic wave of the lead ions. As for the concentration of the supporting electrolyte, we obtained satisfactory results on using 0.025 M solutions of potassium nitrate. At higher supporting electrolyte concentrations, low and poorly reproducible results were obtained during the indirect polarographic determination of sulfate on account of partial precipitation of the latter as the double salt $PbSO_4 \cdot K_2SO_4$, as has been demonstrated by Kolthoff and Pan [4].

A calibration curve which was constructed as described below is shown in the figure: 50 ml lots of potassium sulfate solution with concentrations of O (water), 0.60, 1.00, 1.50, 1.80, and $2.00 \cdot 10^{-3}$ M were placed in 250 conical flasks. To these solutions were added 5.0 ml of 0.5 M potassium nitrate solution, 25.0 ml of ethanol, and 10.0 ml of a 0.2% gelatin solution; the solutions were mixed and 10.0 ml of 10^{-2} M lead nitrate solution added to each of the flasks. After 30 minutes polarograms were taken using a sensitivity of 1/50 (oxygen was removed beforehand from the solutions by means of a hydrogen stream).

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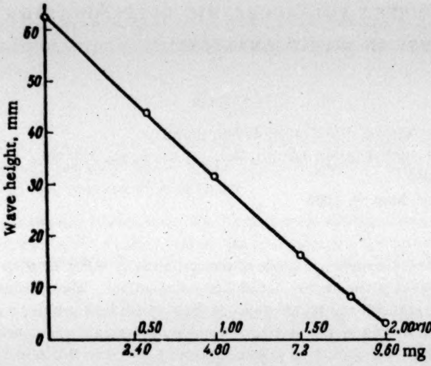
* Translated from English by Z. I. Podgaiskaya.

The calibration curve is a straight line, at least up to a sulfate concentration of $1.75 \cdot 10^{-3}$ M. The break toward the end of the curve is explained by the solubility of the sulfate. From the slope of the linear section of the curve, taking into account that measurements of the polarographic wave of the lead ion can be carried out with an accuracy of 1%, the minimum amount of SO_4^{2-} ions which can be determined is $0.35 \cdot 10^{-3}$ M, the maximum experimental error being 5%. Results of sulfate ion determinations are given in the table.



Calibration curve.

Determination of Sulfate Ions in Water. The method described can be used for the determination of sulfate ions in water. Water, before or after purification, usually contains certain ions which interfere with the precipitation of sulfate ions by lead nitrate in the presence of ethanol; these ions include, e.g., calcium, trivalent iron, chloride, and carbonate ions. The ions indicated can be readily removed by passing the test solution through a column of cation exchange resin, and evaporating the solution obtained, after adding nitric acid and potassium nitrate to it. Addition of nitric acid ensures removal of hydrochloric acid. Potassium sulfate is converted into the sulfate which then serves as the supporting electrolyte.

Determination of Sulfate

SO_4^{2-} taken, mg	SO_4^{2-}, found, mg	Error, %
2.40	2.45	+2.1
	2.36	−1.7
	2.43	+1.2
4.80	4.75	−1.0
	4.75	−1.0
	4.85	+1.0
7.20	7.15	−0.7
	7.17	−0.4
	7.28	+1.1

A description of the method developed for the determination of sulfate in water is given below. The requisite amount of test water is passed through a column packed with the cation exchange resin Amberlite-120 (in the H-form) at the rate of 0.01-0.05 ml/min per ml volume of the cation exchange resin. Fifty ml of the solution which has passed through the column is pipetted into a porcelain basin, and 0.5 ml of concentrated nitric acid and 5 ml of 0.1 M potassium nitrate added; the solution is evaporated to dryness on an electric steam bath. The residue is cooled and 10.00 ml of a 0.04% gelatin solution, 5.00 ml of ethanol, and 5.00 ml of 0.004 M lead nitrate solution added. The solution is transferred to the polarographic cell, oxygen is removed with a hydrogen stream, and polarograms taken at a sensitivity of 1/50. A calibration curve is constructed using known amounts of sulfuric acid.

The calibration curve is a straight line up to a concentration of 34 μg SO_4^{2-}/ml.

The method has been used for determining sulfate ions in purified water obtained from Porte Alegre (Brazil) tap water, containing 18.9 μg SO_4^{2-}/ml. The following values were found: 18.7, 19.1, 18.6, and 19.0 μg SO_4^{2-}/ml (the relative error is respectively 1.1, 1.1, 1.6, and 0.5% SO_4^{2-}).

SUMMARY

An indirect method for the polarographic determination of sulfate is described; it is based on precipitation of sulfate with lead nitrate in an aqueous-alcoholic medium containing 25% ethanol, followed by polarographic determination of excess lead ions. The method has given satisfactory results during the determination of sulfate in water. The water samples are previously freed from interfering ions by passing them through a cation exchange resin, and then evaporating the solutions obtained from the column with nitric acid to eliminate volatile acids, and with potassium nitrate in order to retain the sulfuric acid as sulfate.

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MICRODETERMINATION OF CARBONYL GROUPS BY AN OXIMATION METHOD

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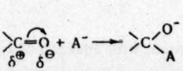
Oximation with hydroxylamine hydrochloride has been in use for a long time for the quantitative macrodetermination of carbonyl groups [1]; $RCOR_1 + NH_2OH \cdot HCl \rightarrow RC(=NOH)R_1 + H_2O + HCl$. In the majority of methods, based on this reaction, which have been suggested, the carbonyl group content is determined on the basis of the amount of hydrochloric acid liberated. Several methods have been described for the macrodetermination of aldehydes and ketones, in which it is suggested that the oximation reaction be carried out in the presence of an organic base, e.g., pyridine [2], N-diethylaminoethanol [3], and octadecenylamine [4].

The micromethod which we should like to suggest for the determination of carbonyl groups is based on oximation with hydroxylamine hydrochloride in the presence of triethanolamine; the latter neutralizes the hydrochloric acid liberated and shifts the equilibrium toward quantitative formation of the oxime. Excess triethanolamine is determined visually or potentiometrically by titration with hydrochloric acid.

Oximation of carbonyl compounds proceeds via an addition stage:

$$(R)(R_1)CO + NH_2OH \rightleftarrows (R)(R_1)C(OH)(NHOH)$$
$$(R)(R_1)C(OH)(NHOH) \longrightarrow (R)(R_1)C:NOH + H_2O.$$

The first, slow stage of the reaction which consists of an addition to the carbonyl group, represents an attack on the carbon of the carbonyl group by a nucleophilic reagent:



and accordingly, the reactivity of the carbonyl group should depend to a marked extent on the value of the positive charge on the carbonyl carbon atom. The greater the positive charge the easier the oximation reaction.

In this connection, oximation of aldehydes with a 0.1 N alcoholic solution of hydroxylamine hydrochloride proceeds very rapidly, even at room temperature. The rate at which ketones are oximated depends markedly on their structure and on the nature of the radicals connected to the carbonyl group. Ketones which have two methylene groups alongside the carbonyl group (i.e., of the type $-CH_2-CO-CH_2-$) are also oximated very rapidly. Ketones which have a methyl group alongside the carbonyl group react more rapidly than ketones which have another alkyl group alongside the carbonyl group; this can be explained by the large inductive effect of higher alkyl radicals, and by an increase in steric hindrance. Taking as an example the oximation of 4,7-dimethyldecanone-5, it is clear how important is the position of the carbonyl group in the ketone molecule (Table 2). On the other hand, an electron-withdrawing group should increase the positive charge of the carbon atom. Thus, p-nitroacetophenone is oximated considerably more readily than acetophenone. Ketones which have a tertiary or quaternary carbon atom alongside the carbonyl group, react fairly slowly. The oximation rate decreases strongly in the case of compounds of the type $>CH-CO-CH<$ or $\succ C-CO-CH<$ and in these cases it is usually necessary to heat with a 0.5 N solution of hydroxylamine hydrochloride.

TABLE 1

Oximation at Room Temperature (0.7 g $NH_2OH \cdot HCl$ in 100 ml of reaction solution)

Test material	Sample wt.	Duration	CO, %		
			calculated	found	difference
Vanillin**	9.356	30 min	18.41	18.45	+0.04
Ditto	9.118	30 "	18.41	18.28	—0.13
Heliotropine**	7.500	30 "	18.66	18.82	+0.16
Ditto	7.455	30 "	18.66	18.68	+0.02
m-Nitrobenzaldehyde**	7.800	30 "	18.53	18.72	+0.19
Ditto	9.628	30 "	18.53	18.69	+0.16
Salicaldehyde**	7.653	30 "	22.94	22.85	—0.09
Ditto	10.418	30 "	22.94	23.16	+0.22
Citral**	4.357	30 "	18.40	18.22	—0.18
Ditto	4.735	30 "	18.40	18.11	—0.29
Methyl ethyl ketone	4.863	30 "	38.85	38.67	—0.18
Ditto	4.622	30 "	38.85	38.55	—0.30
Pinacoline*	5.363	1 hr	27.97	27.74	—0.23
Ditto	5.176	1 "	27.97	27.80	—0.17
2,3-Dimethylheptene-2-one-6**	9.723	30 min	19.98	19.94	—0.04
Ditto	9.505	30 "	19.98	19.84	—0.14
2,6-Dimethylundecanone-10**	6.862	30 "	14.12	14.00	—0.12
Ditto	5.227	30 "	14.12	14.09	—0.03
Phenylacetone**	6.432	30 "	20.88	20.64	—0.24
Ditto	6.205	30 "	20.88	20.58	—0.30
Cyclohexanone**	4.432	30 "	28.54	28.63	+0.09
Ditto	5.058	30 "	28.54	28.52	—0.02
Trans-α-decalone**	4.185	30 "	18.40	18.48	+0.08
Ditto	4.185	30 "	18.40	18.62	+0.22
p-Nitroacetophenone**	8.285	2 hrs	16.96	17.09	+0.13
Ditto	7.847	2 "	16.96	16.87	—0.09
Acetoacetic ester*	6.185	30 min	21.52	21.48	—0.04
Ditto	7.625	30 "	21.52	21.47	—0.05
Ethyl ether of 4-oxo-2-pentene-1-carboxylic acid**	5.160	30 "	17.93	17.95	+0.02
	7.063	30 "	17.93	17.83	—0.10
1,4-Dimethyl-2-keto-cyclopentane-5-carboxylic acid*	6.690	2 hrs	17.93	17.82	—0.11
	7.515	2 "	17.93	17.64	—0.29

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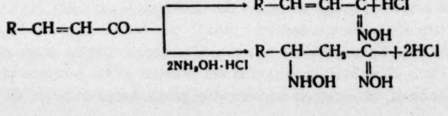
* Visual titration; ** visual titration with addition of sodium chloride.

It has been established [5] that unsaturated ketones which have a system of crossed double bonds (of the type $-CH=CH-CO-CH=CH-$), in contrast to unsaturated ketones with a single double bond (of the type $-CH=CH-CO-$) or diarylketones, are capable of adding on hydroxylamine along the double bond. Such ketones can simultaneously react in two ways, with formation of the oxime of the ketone and the oxime of the hydroxyaminoketone:



The carbonyl content of such ketones cannot be determined by the method suggested.

The suggested method has been used for determining the carbonyl content of various classes of organic compounds: aldehydes, aldoses, ketones, keto acid esters, and also diketones and quinones capable of giving dioximes.

TABLE 2

Oximation at 70-75°

Test material	Sample wt.	$NH_2OH \cdot HCl$ in 100 ml of reaction solution, g	Duration of heating, hr	CO, % calc.	CO, % found	CO, % difference
Galactose*	9.307	0.7	1	15.55	15.25	−0.30
Ditto	7.636	0.7	1	15.55	15.39	−0.16
Glucose*	6.240	0.7	1	14.13	14.25	+0.12
Ditto	5.780	0.7	1	14.13	14.43	+0.30
Acetophenone*	6.017	0.7	1	23.31	23.55	+0.24
Ditto	7.150	0.7	1	23.31	23.19	−0.12
Carvone*	5.427	0.7	1	18.65	18.57	−0.08
Ditto	5.549	0.7	1	18.65	18.39	−0.26
Benzoin**	9.210	0.7	1	13.20	13.24	+0.04
Ditto	8.816	0.7	1	13.20	13.30	+0.10
3(p-methoxyphenyl)2-cyclohexenone-1**	7.983	0.7	1	13.85	13.80	−0.05
	8.580	0.7	1	13.85	13.73	−0.12
2,2-Tetramethylene-5,5-dimethyltetrahydrofuranone-3*	6.930	0.7	1	16.65	16.71	+0.06
	5.599	0.7	1	16.65	16.42	−0.23
2,2-Pentamethylenehexahydrochromanone-4***	7.535	0.7	1	12.60	12.44	−0.16
	9.909	0.7	1	12.60	12.60	0.00
Methyl-α-thienylketone*	4.830	0.7	2	22.20	22.06	−0.14
Ditto	5.222	0.7	2	22.20	22.11	−0.09
Diisopropylketone*	4.185	0.7	3	24.53	24.34	−0.19
Ditto	5.887	0.7	3	24.53	24.24	−0.29
Benzophenone*	7.095	3.5	2	15.37	15.78	+0.41
Ditto	8.146	3.5	2	15.37	15.37	0.00
4,7-Dimethyldecanone-5***	6.626	3.5	3	15.20	15.15	−0.05
Ditto	6.069	3.5	3	15.20	15.49	+0.29
Dimedone*	3.476	0.7	1	39.96	39.94	−0.02
Ditto	4.799	0.7	1	39.96	39.83	−0.13
3-Methoxy-Δ^9-isoestrachryzanenedione-15, 17a***	7.550	0.7	1	18.90	18.87	−0.03
	7.526	0.7	1	18.90	18.81	−0.09
2-Phenylindanedione-1,3***	4.454	3.5	1	25.21	25.65	+0.44
Ditto	4.358	3.5	1	25.21	25.43	+0.22
2,2,6,6-Tetramethyltetrahydropyranedione-3,5***	4.167	3.5	2	32.91	32.74	−0.17
	3.980	3.5	2	32.91	32.92	+0.01
Benzoquinone, 1,4***	2.600	0.7	3	51.83	51.80	−0.03
Ditto	2.570	0.7	3	51.83	51.54	−0.29
α-Naphthoquinone***	3.085	0.7	3	35.42	35.28	−0.14
Ditto	3.080	0.7	3	35.42	35.12	−0.30
1,4-Dimethy-2-ketobicyclo-[2,2,1]-heptane-5-carboxylic acid*	8.219	0.7	2	15.37	15.15	−0.22
	8.190	0.7	2	15.37	15.07	−0.30
2,7-Dimethyl-3-ketobicyclo-[2,2,1]-heptane-5,6-dicarboxylic acid*	8.269	3.5	4	12.38	12.13	−0.25
	9.365	3.5	4	12.38	11.89	−0.49

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* Visual titration; ** visual titration with addition of sodium chloride; *** potentiometric titration.

During attempts to determine the carbonyl group in keto acids and also in the presence of organic acids which do not dissociate strongly, it was established that it is necessary to titrate the reaction solution with hydrochloric acid to a lower pH value than is necessary during determination of other classes of carbonyl compounds; otherwise, high results were obtained during determination of the carbonyl group content. The method described cannot be used for the determination of a carbonyl compound in the presence of organic acids which dissociate strongly.

Experimental. The reaction solution is prepared as follows: 0.7 g (or 3.5 g for preparation of a 0.5 N solution) of hydroxylamine hydrochloride is dissolved in 10 ml of water, 0.5 g of triethanolamine is added, the volume is then made up to 100 ml with 96% ethanol. The indicator is prepared by dissolving 0.1 g of bromophenol blue in 100 ml of 20% ethanol.

Experimental Procedure. Into a 100 ml conical flask with a ground glass stopper is introduced from a buret 5 ml of the reaction solution; an aliquot of test material (3-10 mg) is then added to the flask. Depending on the structure of the test material, the flask is allowed to stand for 0.5-2 hours at room temperature, or a ground glass air condenser is connected to the flask and the latter heated on a water bath at 70-75° for 1-4 hours. A control test is carried out in the same way. When oximation is carried out on heating, on completion of the reaction, the flask is cooled to room temperature. Excess triethanolamine is titrated with 0.02 N hydrochloric visually or potentiometrically.

When a visual indication of the end point is used, three drops of the indicator solution is added in the control experiment, the solution is then titrated with hydrochloric acid until a bluish-green color is obtained (to a lemon-yellow color in the case of determination of carbonyl groups in a keto acid or in the presence of an organic acid). The solution in the flask containing the aliquot of test material is titrated in the same way. In order to compare the color of the solutions in the control and in the test itself, before completing the titration of the test solution, to the latter is added a volume of distilled water which is approximately equal to the difference between the volume of hydrochloric acid used up in titrating the control (a ml) and in titrating the test solution; after addition of the requisite amount of distilled water, titration is continued until the same color as that obtained in the control is reached (b ml).

TABLE 3

Determination of Carbonyl Groups in the Presence of Acids* (0.7 g $NH_2OH \cdot HCl$ in 100 ml of reaction solution)

Test material	Sample wt.	Temp.	Duration of reaction	CO, % calc.	CO, % found	CO, % difference
Vanillin Benzoic acid	6.804 2.200	Room	30 min	13.91	13.84	—0.07
Vanillin Benzoic acid	6.175 3.348	"	30 "	11.94	12.15	+0.21
Acetophenone Acetic acid	4.141 1.845	70—75°	1 hr	16.13	16.01	—0.12
Acetophenone Acetic acid	3.820 1.665	70—75°	1 "	16.23	16.12	—0.11
Cyclohexanone Adipic acid	7.633 2.705	Room	30 min	21.07	21.02	—0.05
Cyclohexanone Adipic acid	4.065 4.922	"	30 "	12.91	12.94	+0.03
Dimedone Succinic acid	4.668 2.240	70—75°	1 hr	27.00	26.91	—0.09
Dimedone Succinic acid	3.110 3.476	70—75°	1 "	18.87	18.67	—0.20

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* Visual titration.

Since the pH of distilled water is considerably higher than the pH of the solution on completion of titration, the amount of hydrochloric acid required to titrate 20 ml of water in the presence of three drops of indicator solution is determined in a separate experiment; on the basis of this experiment a correction (c ml) is calculated for the amount of water added to the flask containing the test aliquot. Titration is carried out in diffused daylight in flasks made of the same type of glass. When 2 ml of a saturated aqueous solution of sodium chloride is added to the contents of the flasks before starting a titration, a more even titration end point is obtained.

The carbonyl group content is calculated by means of the formula:

$$CO, \% = \frac{28.01 \cdot N \cdot (a - b + c) \cdot 100}{m},$$

where N is the normality of the hydrochloric acid and m is the weight of the aliquot in mg.

During potentiometric titration, titration is first carried out visually using an indicator until the greenish-yellow color of the latter is reached (to a pH of about 3.3), the solution is then transferred to a beaker and titrated potentiometrically to a pH of 3.3 using glass and calomel electrodes.

The necessity of the preliminary visual titration is explained by the fact that it is inconvenient to titrate potentiometrically at once in a flask, and, moreover, since the solution being titrated will have a pH within 3.3-3.5 (the volume of the solution at this stage is 10-13 ml) any loss incurred in transferring the solution to a beaker has very little effect on the experimental results.

The carbonyl group content on carrying out a potentiometric titration is calculated by means of the formula:

$$CO, \% = \frac{28.01 \cdot N (a - b) \cdot 100}{m},$$

where N is the normality of the hydrochloric acid; a is the volume of hydrochloric acid used in titrating the control, ml; b is the volume of hydrochloric acid used in titrating the test solution; and m is the weight of aliquot, mg.

Potentiometric titration is recommended in those cases where the solution to be titrated is colored, and also if it is turbid.

It has been found that when a 0.1 N solution of hydroxylamine hydrochloride is used the accuracy of the method is about ± 0.3%, while when a 0.5 N solution of hydroxylamine hydrochloride is used the accuracy of the method drops to ± 0.5%.

Tables 1-3 contain results of the analyses of carbonyl compounds by the suggested method.

SUMMARY

A method has been developed for the microdetermination of carbonyl compounds by oximation with hydroxylamine hydrochloride in the presence of triethanolamine. The method can be used for the determination of carbonyl groups in aldehydes, ketones, keto acids, keto acid esters, and also in diketones and quinones which can form dioximes.

It has been established that it is possible to determine carbonyl compounds in the presence of organic acids which only dissociate to a small extent.

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QUANTITATIVE DETERMINATION OF MONOSUBSTITUTED 1-, 3-, 4- OXADIAZOLES BY POTENTIOMETRIC TITRATION WITH SODIUM NITRITE

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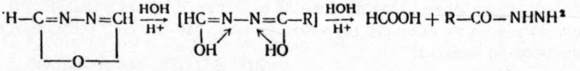
In recent years derivatives of 1-, 3-, 4-oxadiazole have found increasing application in pharmacy [1], in dye production [2], and in scintillation techniques [3]. Hitherto, as far as we are aware, however, no methods have been published on their quantitative determination. In this connection, therefore, we have developed a method for the quantitative determination of 2-substituted derivatives of 1-, 3-, 4-oxadiazole.

During a study of chemical reactions in the 1-, 3-, 4-oxadiazole series [4], it was found that monosubstituted derivatives of 1-, 3-, 4-oxadiazole readily interact with sodium nitrite even in the cold in aqueous solutions of mineral acids, to form reaction products which are sparingly soluble in this medium. In the course of a more detailed study of this reaction it was found that it proceeds in two stages. In the first stage, acid hydrolysis of the monosubstituted 1-, 3-, 4-oxadiazole to the corresponding primary hydrazide and formic acid occurs according to the following scheme:



$$H{-}C{=}N{-}N{=}CH \xrightarrow[H^+]{HOH} [HC{=}N{-}N{=}C{-}R] \xrightarrow[H^+]{HOH} HCOOH + R{-}CO{-}NHNH^2$$

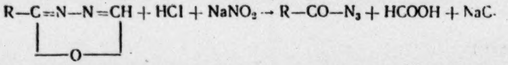
It was established that hydrolysis proceeds almost instantaneously – immediately after dissolving the test material in acid. Thus, we isolated the hydrolysis products of 2-phenyl-1-, 3-, 4-oxadiazole, and 2-(p-nitrophenyl)-1-, 3-, 4-oxadiazole, these proved to be identical in elemental composition and melting point with the corresponding benzhydrazide and p-nitrobenzhydrazide.

The second stage consists of the further interaction of the primary hydrazide with nitrous acid according to the well-established reaction with formation of the corresponding azide:

$$R{-}CO{-}NHNH_2 + HNO_2 \rightarrow R{-}CO{-}N_3 + 2H_2O$$

The precipitated azides were identified by means of their elemental composition, melting point, and other properties as well (their ready solubility in diethyl ether, their insolubility in water, their tendency to explode on melting). Thus, 2-phenyl-1-, 3-, 4-oxadiazole gave benzoylazide, while 2-(p-nitrophenyl)-1-, 3-, 4-oxadiazole gave p-nitrobenzoylazide, and 2-(p-tolyl)-1-, 3-, 4-oxadiazole gave p-tolylazide, etc.

Thus, the over-all interaction between monosubstituted derivatives of 1-, 3-, 4-oxadiazole with sodium nitrite in an acid medium can be expressed by the general equation:



$$\mathrm{R{-}\underbrace{C{=}N{-}N{=}CH}_{O} + HCl + NaNO_2 \rightarrow R{-}CO{-}N_3 + HCOOH + NaCl}$$

As is clear from this equation monosubstituted derivatives of oxadiazole react under the given conditions with sodium nitrite in equimolar amounts. The reaction proceeds rapidly on the whole, and, as was demonstrated, it proceeds quantitatively, thanks to which it can be used for the potentiometric titration of 2-substituted derivatives of 1-, 3-, 4-oxadiazole.

The test materials which were used for the potentiometric work, and whose synthesis has been described [4, 5], were purified by vacuum distillation (low melting) until they gave constant absorption spectra, and by recrystallization or by passing through a chromatographic column; the treatment used depended on the individual properties of each test compound.

Measurements were carried out on the LP-5 tube potentiometer of the MOSKIP factory. A saturated calomel electrode was used as the null electrode, and a bright platinum electrode as the indicator electrode. The sodium nitrite solution was standardized potentiometrically against p-nitraniline and sulfanilic acid [6]. This solution was kept in a dark colored hermetically sealed flask. Titration was carried out from a buret, the drawn-out tip of which was immersed in the solution being titrated. During a determination, the sodium nitrite was initially added in large aliquots, while as the end point came nearer the aliquots of titrant added were decreased until their volume was equal to a half scale division on the buret.

An aliquot of test material was usually dissolved in concentrated hydrochloric acid which was subsequently diluted two-three times with distilled water. As control tests showed, the acid concentration does not affect the experimental accuracy essentially. It was found possible to titrate sparingly soluble oxadiazoles in a mixture of hydrochloric and glacial acetic acid with the preliminary heated solution of the test sample.

The potential was rapidly established at the beginning of titration, while toward the end it took 3-4 minutes to be established. Addition of KBr as a catalyst, a technique which has been successfully used for the potentiometric titration of aromatic amines [6], and of hydrazides as well [7], with sodium nitrite, was found to have almost no effect on the rate at which the potential was established in the given instance. During the first moments after addition of each new portion of titrant there was observed an instantaneous increase in the potential, this was followed by a gradual drop to a known established value; this is explained by an accumulation of NO_2^- ions in the first moments, as has been shown during the titration of amines [6, 8] and hydrazides [7]. The potential jump for the compounds which we examined lay within the range 640-730 mv, accordingly, the approach of the end point can always be observed.

The experimental accuracy is about 1% (see table).

Determination of Certain Oxadiazoles

1-, 3-, 4-Oxadiazole	Sample wt. mg	Found, %	Error, %
2-Phenyl-	46.6	100.3	0.3
2-(p-Nitrophenyl)-	32.8	101.1	1.1
2-(p-Tolyl)-	23.3	99.0	1.0
2-(p-Methoxyphenyl)-	23.4	99.2	0.8
2-(p-Aminophenyl)-	55.0	101.3	1.3
2-(p-Dimethylaminophenyl)-	2.0	99.2	0.8
2-(p-Carbethoxyphenyl)-	3.2	98.8	1.2

When the oxadiazole molecule contains a group which is also capable of quantitatively interacting with sodium nitrite, as in the case of 2-(p-aminophenyl)-1-, 3-, 4-oxadiazole, double the amount of sodium nitrite is used, as is the case during titration of aminobenzhydrazides [7].

Since good results are also obtained with amounts of test materials amounting to 10^{-5} mole, the method can be used both as a macro- and microvariant without modifying the method essentially.

Experimental Procedure. An aliquot (0.01-0.1 mM) of the monosubstituted 1-, 3-, 4-oxadiazole is dissolved in concentrated hydrochloric acid, and, in the case of readily soluble oxadiazoles, the solution is diluted with 2-3 times its amount of water. For the determination of sparingly soluble compounds, it is expedient to add some glacial acetic acid, or to heat the solution with the sample. Next, with vigorous stirring, large aliquots (0.5-1 ml) of titrant are added initially from a buret whose tip is immersed in the solution being titrated; the size of the aliquots of 0.01 N sodium nitrite is decreased (0.1-0.01 ml) as the end point is approached. The end point corresponds to the maximum increase in the potential $\Delta E/\Delta V$, where ΔE is the difference in mv between two successively added portions of sodium nitrite, and ΔV is the volume of the portion of sodium nitrite added.

The reaction product — the corresponding aroylazide — which separated out during titration does not interfere with the determination.

The gram-equivalent of the monosubstituted 1-, 3-, 4-oxadiazole which is being titrated is numerically equal to its molecular weight.

SUMMARY

A method has been developed for the quantitative determination of monosubstituted 1-, 3-, 4-oxadiazoles in which the latter are potentiometrically titrated with sodium nitrite. The determination can be carried out on a macro as well as a micro scale. A study has been made of the chemical reactions of monosubstituted 1-, 3-, 4-oxadiazoles during their titration with sodium nitrite in an acid medium.

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DETERMINATION OF SUGARS BY DIRECT TITRATION WITH AN ALKALINE SOLUTION OF THE COPPER COMPLEX OF TRIHYDROXYGLUTARIC ACID

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Classical methods [1-3] of determining sugary materials use Fehling's solution, which consists of an alkaline solution of the copper complex of tartaric acid [4]. The main difficulty connected with the use of this solution is the fact that no proportionality is observed between the amount of cuprous oxide formed and the amount of sugary material in solution. We have described macro- [5] and micromethods [6] for the permanganometric determination of sugars by means of the copper complex of xylotrihydroxyglutaric acid. It was found that on replacing Fehling's solution by an alkaline solution of the copper complex of trihydroxyglutaric acid, under the conditions which we had established, there is a strict proportionality between the amount of sugar and the amount of cuprous oxide formed.

Direct titration of sugars is widely used in industry, although this method suffers from greater drawbacks than the permanganometric or gravimetric methods. In Soxhlet's first variant [1] Fehling's solution was heated in an open basin and the sugar solution added to it until complete reduction of cupric to cuprous was achieved. Heating the solution in a flask, which enables one to depress the reverse oxidation of cuprous oxide by atmospheric oxygen, and the use of external indicators (potassium ferrocyanide, sodium thiosulfate) significantly increase the accuracy of the method. The use of external indicators, however, demands that boiling be stopped and leads to expenditure of test liquid. This drawback was eliminated by Lane and Eynon [7] who added methylene blue as an internal indicator to the Fehling solution. In order to prevent overheating of the liquid and to prevent oxidation of cuprous oxide by atmospheric oxygen, it has been suggested that the sugar solution be added to the flask containing the Fehling solution, steam being passed through it continuously. When such a technique is used, separation of suspended cuprous oxide, which is bright-red in color, interferes considerably with the end point. It has been found that addition of potassium ferrocyanide to the Fehling solution eliminates separation of cuprous oxide [8-12].

Despite all these improvements, the direct titration method still has some disadvantages which are related to the nature of the Fehling solution itself. They reduce to the fact that the oxidation of the sugars cannot be subjected to stoichiometric calculations (Table 1). It is only possible to assume a more or less satisfactory inverse proportionality between the volume of solution containing the reducing sugars and its concentration, over a narrow concentration range. Accordingly, in the well-known methods of Lane and Eynon [7], and Nizovkin and Emel'yanova [11], etc., it is recommended that two operations always be carried out, from the first operation an approximate idea is obtained how much the solution should be diluted so that its concentration lies within this narrow range. When an alkaline solution of cupritrihydroxyglutarate is used there is no need for this operation. As can be seen from Table 1, there is a strict inverse proportionality between the volume of sugar solution used in the titration, and its concentration. Consequently, there is no need to carry out an approximate determination.

The present article contains results on the determination of pure monosaccharides: glucose, fructose, galactose, mannose, xylose, and, in addition, invert saccharose in solutions of varying concentration. This method permits sugar to be determined in fruits, fruit juices, wines, confectionary, pentose and hexose hydrolyzates, etc. A statistical treatment of the results has shown that the method has a high degree of accuracy in all cases.

TABLE 1

Sugar	Conc. of sugar solution g/liter	Amt. sugar soln. used for titrating 10 ml of Fehling's soln. ml (mean of 4 determinations)	For titrating 10 ml of cupritrihydroxyglutaric acid solution			Probable deviation of the mean result, $S_{\bar{x}}$
			no. of expts.	sugar solution used, ml	amt. of sugar used, mean value, mg	
Glucose	1.000	5.70	9	6.00— 6.10	6.05	0.0090
	0.500	5.79	9	12.05—12.15	6.05	0.0042
	0.333	5.84	9	18.10—18.20	6.05	0.0034
Fructose	1.000	5.90	4	6.20— 6.25	6.21	0.0126
	0.500	6.17	4	12.40—12.45	6.21	0.0072
	0.333	6.40	4	18.60—18.65	6.21	0.0040
Galactose	1.000	6.43	4	6.85— 6.90	6.89	0.0125
	0.500	6.59	4	13.75—13.80	6.89	0.0063
	0.333	7.04	4	20.65—20.70	6.89	0.0049
Mannose	1.000	5.88	4	6.30— 6.35	6.34	0.0127
	0.500	6.06	4	12.65—12.70	6.34	0.0063
	0.333	6.19	4	19.00—19.05	6.34	0.0049
Invert saccharose	1.000	5.60	9	5.80— 5.85	5.84	0.0074
	0.500	5.68	4	11.65—11.70	5.84	0.0072
	0.333	5.80	4	17.50—17.55	5.84	0.0049
Xylose	1.000	5.67	9	6.05— 6.15	6.10	0.0118
	0.500	5.75	9	12.15—12.25	6.10	0.0042
	0.333	5.96	9	18.25—18.30	6.10	0.0019

The following solutions are used for the determination.

Solution No. 1. 10.000 g of $CuSO_4 \cdot 5H_2O$ (chemically pure grade recrystallized from water) is accurately weighed out and dissolved in water, 0.04 g of methylene blue is added. The volume of the solution is accurately made up to one liter.

Solution No. 2. 32 g of trihydroxyglutaric acid,* 90 g of sodium hydroxide, and 4 g of potassium ferrocyanide – $K_4[Fe(CN)_6] \cdot 3H_2O$ are dissolved in water and the volume made up to one liter. If the solution thus prepared is not clear enough, it is filtered through a No. 3 glass crucible or through glass wool.

By pouring together equal volumes of these two solutions an alkaline solution of cupritrihydroxyglutaric acid is obtained.

Analytical Procedure. Determinations were carried out in the apparatus shown in the diagram, this can be replaced by an even simpler homemade apparatus [13].

Five ml each of solution No. 1 and solution No. 2 are introduced into the inner vessel. At the same time 250-300 ml of water are heated to the boil in vessel 2. When the water in the flask is boiling, the inner flask with the solution of the copper complex is fitted into it mounted in a stopper. When vessel 1 has heated up enough, steam starts to pass through the solution and causes it to boil evenly. Excess steam from the inner vessel passes out through 3 in the neck of vessel 1. Clip 4 is used for regulating the pressure inside the conical flask 2.

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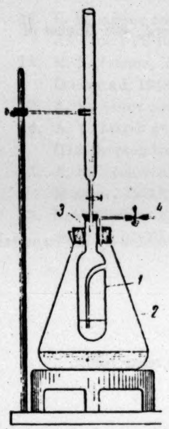
* Acid, "for foodstuffs" grade produced by the hydrolysis industry [6] can be used.



1) Inner vessel; 2) outer vessel; 3) exit for steam from the inner vessel; 4) rubber valve with clip.

When the solution of the copper complex starts to boil, the liquid whose sugar content it is desired to determine is added from the buret at the rate of 3-4 drops per second until the blue color of the liquid in the inner flask turns violet. Starting at this point, one waits for two minutes and then continues to titrate at the rate of one drop per 5-6 seconds (not quicker) until there is a sharp change from violet to a weak-yellow which indicates the end point. A determination normally takes 4-5 minutes.

Determination of Glucose and Other Monosaccharides. Chemically pure grade sugar which had been dried beforehand to constant weight at 40-60° was used. Titration was carried out from a buret whose scale divisions had an accuracy of 0.02 ml. The standard vessel was calibrated with water.

The experimental results are given in Table 1.

Determination of Sugary Materials in Industrial Products by the Method of Additions. Samples of industrial products were prepared according to published instructions [11, 14, 15, 16]. The content of sugary material was calculated by means of the formula: $x = k/V$ mg/ml, where V is the number of ml of sugar solution used up in the titration, while k is the titer of 10 ml of copper complex solution; k for the various sugars has, under the operational conditions indicated above, the values given in Table 1; for glucose e.g., the value is 6.05.

Table 2 contains the sugar content expressed as mg per g of solid product (e.g., apples, caramel), or in mg per ml of liquid product (juice, wine).

TABLE 2

Product tested	Sugar added	One liter of solution contained		Ml of soln. used for titrating 10 ml of the copper complex	Sugar found (mean value) in mg/g of product (or mg/ml respectively)	Dispersion	Accuracy	Probable relative error, %
		technical product	added sugar (g)					
"Kal'vil' White Winter" apples	glucose	2.000 g	0	24.90—24.95	121.4	0.02	0.2	0.16
			0.250	12.25—12.30	121.2	0.25	0.8	0.3
			0.500	8.13—8.15	121.4	0.23	0.8	0.2
"Rkatsiteli" grape juice	glucose	5.00 ml	0	6.40—6.45	188.3	0.7	1.4	0.7
			0.250	5.05—5.10	188.5	1.6	2.0	0.8
			0.500	4.15—4.20	189.0	2.9	2.7	0.9
"Muscat Moldavain Desert wine	invert saccharose	5.00 ml	0	7.90—8.00	146.9	0.6	1.2	0.8
			0.250	5.90—5.95	146.7	0.7	1.3	0.7
			0.500	4.70—4.75	147.1	2.3	2.4	1.0
"Teatral'naya" caramel	glucose	4.000 g	0	7.10—7.15	212.0	0.5	1.2	0.5
			0.250	5.50—5.55	211.9	1.6	2.0	0.7
			0.500	4.45—4.50	212.1	3.1	2.8	0.8
"Vesna" confectionary	invert saccharose	2.000 g	0	4.55—4.60	638.3	14	6.0	0.9
			0.250	3.80—3.85	638.5	33	9.2	1.2
			0.500	3.25—3.30	638.4	46	10.7	1.2
Corn stalks (pentose hydrolyzate)	xylose	2.500 g	0	6.40—6.45	379.0	2.2	2.4	0.6
			0.250	5.10—5.15	377.2	5.8	3.8	0.8
			0.500	4.20—4.25	379.2	11.6	5.4	0.9
Corn stalks (hexose hydrolyzate)	glucose	2.500 g	0	8.30—8.35	290.3	0.8	1.4	0.5
			0.250	6.20—6.25	289.6	2.4	2.5	0.6
			0.500	4.90—4.95	290.4	5.8	3.8	0.6

These results are the mean of four determinations. When the method of additions was used, the amount of sugar added was subtracted from the sugar content found by titration.

The mean square error of a single determination (dispersion)

$$s^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1},$$

is also given where n is the number of determinations; the accuracy of the method calculated by the formula:

$$h = t_\alpha \cdot s_{\bar{x}}$$

is given for α (confidence) = 0.95. Here $s_{\bar{x}} = \frac{s}{\sqrt{n}}$ is the probable deviation of the mean result.

The probable relative error is given in %:

$$\frac{s_{\bar{x}} \cdot t_{0.95}}{a} \cdot 100$$

In most cases the probable relative error does not exceed 1%.

SUMMARY

A new method is suggested for the direct titration of sugary materials by means of an alkaline solution of the copper complex of trihydroxyglutaric acid. It has been established that, in contrast to methods based on the use of Fehling's solution, there is a strict inverse proportionality between the volume of solution used up in a titration and its concentration.

It has been shown that the method can be used for the determination of sugary materials in fruits, fruit juices, wines, confectionary, pentose and hexose hydrolyzates with a high degree of accuracy.

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QUANTITATIVE DETERMINATION OF IMPURITIES IN ADIPONITRILE

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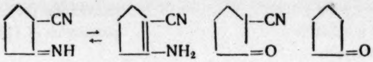
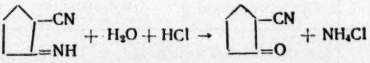
One of the intermediate products during the production of polyamide resins is adiponitrile (the dinitrile of adipic acid). In order to obtain high quality polyamide resins, only minimum amounts of impurities can be permitted in the adiponitrile. In a previous paper [1] it was shown that the main impurities in adiponitrile are 1-imino-2-cyanocyclopentane or 1-amino-2-cyanocyclopentene-1,2 (I), 2-cyanocyclopentanone-1 (II), and cyclopentanone (III).



I II III

There are no published methods for the quantitative determination of impurities in adiponitrile. Indirect methods have been used for getting an indication of the purity of adiponitrile: setting point, color, permanganate number, acidity, etc. [1].

We have developed a method for the quantitative determination of impurities in adiponitrile. The basis of the method is an acidimetric determination of 1-imino-2-cyanocyclopentane (I), and a polarographic determination of 2-cyanocyclopentanone (II) and cyclopentanone (III). The cyanimine is not reduced on a dropping mercury electrode. Its determination is based on the fact that its molecule contains the readily hydrolyzed imine group. Hydrolysis is effected with weak hydrochloric acid:



The cyanoimine (I) content of the adiponitrile is determined by back titrating the excess hydrochloric acid. Using the Chugaev-Zerewitinov method the amount of active hydrogen in the cyanoketone was found to be the theoretical value. It follows from this that the cyanoketone (II) enolizes readily. It is also possible that the equilibrium between the keto- and enol-forms in this compound is shifted toward the latter. In II the nitrile group is conjugated with the double bond. It is known [2] that such compounds are reduced on a dropping mercury electrode. Experiments showed that 2-cyanocyclopentanone-1 (II) is actually reduced at $E_{1/2} = -2.0$ v with respect to the saturated calomel electrode (S.C.E.). Cyclopentanone (III), like other ketones [3] is reduced at a very negative potential $E_{1/2} = -2.6$ v (S.C.E.)., and this strongly complicates its determination. At high cyclopentanone concentrations in the liquid which is being polarographed (about 0.06%) a maximum appeared which we were unable to suppress. The half-wave potentials of the cyanoketone (II) and cyclopentanone (III) differ strongly from each other (Fig. 1). This means that it is possible to determine the cyanoketone (II) and cyclopentanone (III) quantitatively in each others presence.

The electrical reduction of 2-cyanocyclopentanone-1 (II) and cyclopentanone (III) was studied on a M-8 type polarograph of Gor'ky University. The galvanometer sensitivity was $2.79 \cdot 10^{-9}$ amp/mm, while the capillary characteristic was $m^{2/3} \cdot t^{1/6} = 1.384$ mg$^{2/3}$ sec$^{-1/2}$. All the tests were made at 25 ± 0.3°. Adiponitrile which had been purified by the sulfuric acid-permanganate method [4] followed by an additional treatment with ammonium bisulfite, was used for the work. Twice distilled isopropanol was used. The test compounds were synthesized by methods published previously [1].

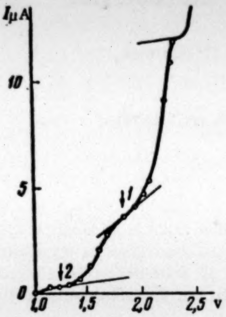


Fig. 1. Polarograms for a 0.042% solution of cyclopentanone (1) and a 0.025% solution of 2-cyanocyclopentanone-1 (2) in a supporting electrolyte of 0.1 N tetraethylammonium iodide solution.

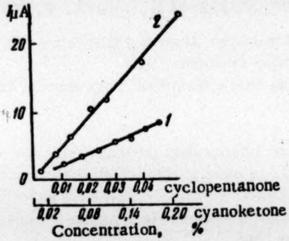


Fig. 2. Calibration lines for cyclopentanone (1) and 2-cyanocyclopentanone-1 (2).

The solution in which the reduction of the cyanoketone (II) and cyclopentanone (III) on a dropping mercury electrode was studied, contained 40% of adiponitrile and 35% of isopropanol. This enabled down to 0.005% of impurity to be determined. The isopropanol served for homogenizing the adiponitrile and the aqueous solution of the supporting electrolyte. Tetraethylammonium iodide at a concentration of 0.1 N in the solution being polarographed was used as the supporting electrolyte. From the fact that the ratio I_d/C (Table 1) is constant for the concentration range studied, it follows that the wave heights for cyanoketone (II) and cyclopentanone (III) are proportional to their concentrations.

TABLE 1

2-Cyanocyclopentanone-1 (II)		Cyclopentanone (III)		2-Cyanocyclopentanone-1 (II)		Cyclopentanone (III)	
Concentration, %	I_d/C	Concentration, %	I_d/C	Concentration, %	I_d/C	Concentration %	I_d/C
0.011	107	0.012	179	0.086	116	0.030	180
0.032	113	0.018	174	0.108	113	0.041	173
0.054	110	0.024	179	0.216	109	0.046	176

Experiments were carried out within the concentration ranges (in the solution being polarographed) 0.005-0.22% for the cyanoketone (II) and 0.01-0.06% for cyclopentanone (III).

The possibility of simultaneously determining 2-cyanocyclopentanone (II) and cyclopentanone (III) was checked within the concentration ranges indicated above. It was found that the ratio of the concentrations, in percent, for the cyanoketone (II) and cyclopentanone (III) should not be greater than 1 : 2. In this case, the wave height for cyclopentanone (III) does not depend on the presence of (II). The presence of cyclopentanone

(III) in any concentrations does not affect the value of the limiting current of the cyanoketone (II). Adiponitrile and 1-imino-2-cyanocyclopentanone (I) do not change the values of the limiting current for the cyanoketone (II) and cyclopentanone (III) over a wide concentration range.

Method for Determination of Cyanoimine (I), Cyanoketone (II), and Cyclopentanone (III). In order to determine 1-imino-2-cyanocyclopentane an aliquot of adiponitrile (about 10 g) is placed in a 100 ml conical flask. Fifteen ml of isopropanol and 20-25 ml of water are added. Five ml of a 0.005 N HCl is added with a pipet and the solution well mixed by shaking. Excess HCl is then titrated with 0.005 N NaOH using bromothymol blue as indicator. The 1-imino-2-cyanocyclopentane content (in %) is calculated by means of the formula:

$$\frac{108\,(V_1K_1 - V_2K_2)N \cdot 100}{q \cdot 1000},$$

where 108 is the mol. wt. of 1-imino-2-cyanocyclopentane; V_1 is the volume of 0.005 N HCl taken for hydrolysis; V_2 is the volume of 0.005 N NaOH used in the titration; N is the normality of the acid and alkali; K_1 and K_2 are corrections for the acid and alkali titers; q is the weight of the aliquot taken in g.

To determine the cyanoketone (II) and cyclopentanone (III), 10 ml of adiponitrile is placed in a 25 ml standard flask. To this flask is added by means of a pipet 5 ml of a 0.5 M aqueous solution of tetraethylammonium iodide and 7 ml of isopropanol. The contents of the flask are carefully mixed and made up to the mark with water. The solution to be polarographed is swept with nitrogen for 15 minutes. Polarograms are taken with a capillary with a slow drop rate, the anode is a mercury pool. The minimum concentrations of the impurities which can be determined in adiponitrile by the method developed are as follows: the cyanoimine (I) – 0.001%; the cyanoketone (II) – 0.008%; and cyclopentanone (III) – 0.01%. A determination does not take longer than 40 minutes. The content of the cyanoketone (II) and cyclopentanone (III) is determined by means of calibration lines constructed beforehand (Fig. 2). The method was checked by analyzing a series of synthetic mixtures (Table 2).

TABLE 2

Cyanoimine (I), %			Cyanoketone (II), %			Cyclopentanone (III), %		
taken	found	deviation	taken	found	deviation	taken	found	deviation
0.022	0.023	+0.001	0.021	0.019	–0.002	0.041	0.041	—
0.015	0.014	–0.001	0.015	0.016	+0.001	0.033	0.032	–0.001
0.011	0.011	—	0.012	0.012	—	0.028	0.027	–0.001
0.0022	0.0022	—	0.010	0.010	—	0.024	0.024	—
0.0011	0.0010	–0.0001	0.003	0.003	—	0.021	0.019	–0.002

The method developed has been used for the analysis of samples of adiponitrile purified by various methods.

SUMMARY

The conditions for the reduction of 2-cyanocyclopentanone-1 and cyclopentanone on a dropping mercury electrode have been studied.

A method has been developed for the simultaneous quantitative determination of 1-imino-2-cyanocyclopentane, 2-cyanocyclopentanone-1, and cyclopentanone in adiponitrile.

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COPRECIPITATION OF TUNGSTEN WITH FERRIC HYDROXIDE

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It has been indicated in the literature that it should be possible to coprecipitate small amounts of tungstate ions with ferric hydroxide [1-3]. In some cases the coprecipitation has been regarded as complete [1], while in other cases it has been indicated that only 70-79% of the tungsten is coprecipitated [3]. There is no published information on the relation between completeness of coprecipitation of tungsten and the various conditions under which the process is carried out.

Coprecipitation of tungstate ions with ferric hydroxide was studied with the aid of the radioactive isotope W^{185}. The distribution of tungsten between the solution and precipitate was determined on the basis of the radioactivity of the dry residue obtained after evaporating part of the solution (0.200 ml) in a platinum basin; the radioactivity was measured with a T- 25 BFL torsion counter on a B-2 setup. The precipitate was separated from the solution of centrifugation, while the pH of the solution was measured with two glass electrodes on a LP-5 pH-meter. The ionic strength of the solution containing ammonium chloride amounted to 0.2, 1.0, and 2.0 in individual series of experiments. The time for which the solution was in contact with the precipitate was 30 minutes, as a rule. The volume of the solution was 20.0 ml, while the temperature was 18°.

It is known [4-6] that when natural tungsten is bombarded with neutrons, in addition to W^{185}, the long life W^{188} isotope ($T_{1/2}$ = 65 days) may be obtained as a result of the successive capture of two neutrons by the W^{186} isotope; the W^{188} isotope, as a result of β-decay, then gives the rhenium isotope Re^{188} which possesses very hard β- and γ-radiation. It has been shown earlier [7] that the insignificant amount of the Re^{188} isotope present as an impurity in W^{185}, can lead, under certain conditions of measuring the activity of the W^{185} – such that conditions may arise which cause a large absorption of the soft β-radiation of W^{185} – to some distortion of the results when the behavior of tungsten is controlled on the basis of the W^{185} isotope. It has also been shown that results of a photometric determination of tungsten in solution by the thiocyanate method do not always completely coincide with the results of radiometric determinations of tungsten in the same solution, probably, because the change in color of the thiocyanate complex of tungsten with time is not recorded sufficiently accurately, although the absence of a definite limiting amount of tungsten in solution can be observed by this method.

Bearing in mind what has been said above, the activity of E^{185} was measured at a minimum distance of the precipitate from the counter window (8 mm), and at an original activity of the preparation of 1800-2600 cpm. The standard and the test sample were always dried at the same temperature (96°) and in the course of the same time, while the salt composition of the standard and test solution was also the same. Under these conditions the experimental error arising from the presence of Re^{188} was less than 0.5%; this was determined on the basis of the absorption of the radiation by aluminum and on the basis of the activity of the solution after complete coprecipitation of tungstate ions with ferric hydroxide. Completeness of coprecipitation in a series of experiments was controlled by photometric determination of tungsten in solution (thiocyanate method) as well as by measurement of the radioactivity of the solution.

From the measurements of the radioactivity of solutions by various methods it was found that in the pH range starting with the pH at which coagulation of the precipitate starts, to pH 7.7, coprecipitation of tungstate ions with ferric hydroxide proceeds quantitatively, when the activity was measured with a T-25 BFL counter under the conditions indicated above (Curve 1, Fig. 1). When the MST-17 counter was used, and the distance between the counter window and the sample, and the amount of salt in solution increased, it was necessary to increase the amount of radioactive tungsten added to the potassium tungstate, while at the same time the fraction of Re^{188} in solution increased, and this led to an increase in the difference between the actual value of the coprecipitation (100%) and that measured to 6% (Curves 2 and 3).

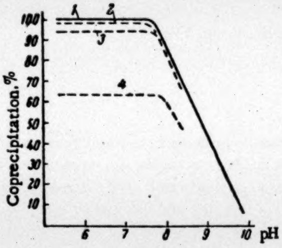

Fig. 1. The apparent value of the coprecipitation of tungstate ions with ferric hydroxide, as a function of the conditions used for measuring the activity.

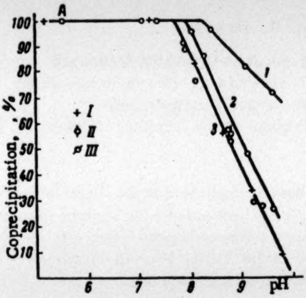

Fig. 2. Coprecipitation of tungsten with ferric hydroxide when the various solutions are added in different orders, and for variations in the ammonium salt concentration. W = 1 mg; Fe = 0.1 mg-atom; $[NH_4Cl] = 1$ M; T = 30 min; I) W = = 100 μg; $[NH_4Cl] = 0.2$ M; II) $[NH_4Cl] =$ = 0.2 M; III) $[NH_4Cl] = 2$ M; 1) $Fe(OH)_3$ precipitated in the presence of K_2WO_4; 2) $FeCl_3$ added to a mixture of K_2WO_4 and NH_4Cl solutions; 3) K_2WO_4 added to freshly precipitated $Fe(OH)_3$.

On measuring the activity of the solution in a glass cuvette with an AS-1 counter, this difference can be as much as 40% (Curve 4). The technique indicated above for measuring the W^{185} activity almost excludes the effect of Re^{188}, present as an impurity, on the experimental results.

Coprecipitation of tungstate ions with ferric hydroxide in an alkaline medium depends on the pH of the medium and also on the order in which the solutions are poured together (Fig. 2). Coprecipitation,which is a maximum on precipitating ferric hydroxide in the presence of tungstate ions (Curve 1), decreases on precipitating the carrier by pouring ferric chloride into an alkaline solution containing tungstate (Curve 2), and is at a minimum on adding potassium tungstate to freshly precipitated ferric hydroxide. In all the cases indicated the time for which the precipitate was in contact with the solution was 30 minutes.

Thus, coprecipitation and 1 mg of tungsten (and 100 μg W, Curve 3) is quantitative in the pH range starting from the pH at which coagulation of the precipitated commences, to pH 7.7-8.2. Tungsten is also completely coprecipitated when the carrier is precipitated with pyridine (point A). Changes in the ammonium chloride concentration from 0.2 to 2.0 M do not affect the extent to which tungsten is coprecipitated with ferric hydroxide, which testifies to the chemosorptive nature of the coprecipitation of tungstate ions with ferric hydroxide, this is presumably related to the formation of sparingly soluble tungstates on the surface of the hydroxide precipitate. Some authors have shown that,at a pH less than 7, various forms of the tungstate ions may be present in solution, including polymeric tungstate ions. Independently of the composition and charge of these ions, their coprecipitation with ferric hydroxide is complete over a wide pH range. WO_4^{2-} ions are found in the alkaline region, this is confirmed, in our opinion, by the slope of Curve 1, Fig. 2, and the slope of similar coprecipitation curves for SO_4^{2-}, HPO_4^{2-}, CrO_4^{2-}, MoO_4^{2-} ions with ferric hydroxide under identical conditions.

Sorption of tungstate ions by the surface of the ferric hydroxide precipitate on adding potassium tungstate to freshly precipitated ferric hydroxide, increases with an increase in the time for which the precipitate is in contact with the solution (Fig. 3). During adsorption of chromate ions by ferric hydroxide, maximum coprecipitation is reached in the course of the first minute [7]; with time there occurs a slow decrease in adsorption, presumably, as a result of the crystallization of the carrier precipitate. In similar experiments on the coprecipitation of tungstate ions with ferric hydroxide, there is at first a rapid, and then a slow absorption of tungstate ions by the carrier precipitate. Maximum sorption is achieved in the course of the first 10-15 hours for which the solution is in contact with the precipitate (Curve 3); the percentage sorption does not change in the course of the subsequent 30-50 hours.

Vikt. I. Spitsyn [8] has shown that on decreasing the pH of the medium to 8-6, the tungstate ions are converted into paratungstate ions. Under our conditions (pH 8-10) this process, probably, does not occur in solution, nevertheless, the increase in the sorption of tungstate ions by the negatively charged precipitate of ferric hydroxide in the pH range indicated testifies to the occurrence of a chemical process which leads to an increase in coprecipitation of tungsten. Such processes could be: the slow penetration of tungsten ions right into the hydroxide precipitate with formation of iron tungstates; the formation in solution, or on the precipitate surface, of aquopolyanions of tungsten. The first of the processes indicated is the least likely, since experiments have shown that about 10-15% of chromate ions coprecipitated with ferric hydroxide, on precipitation of the carrier in the presence of the anion, cannot be extracted from the precipitate without dissolving the carrier, since the diffusion processes within the ferric hydroxide micelles, apparently, proceed very slowly.

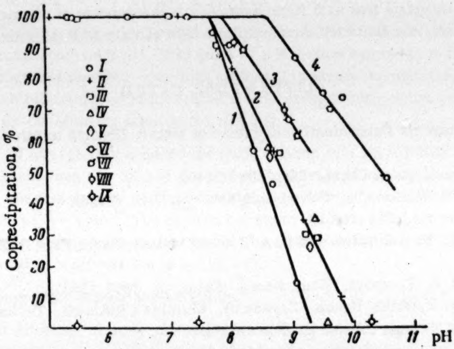

Fig. 3. Effect of time on the coprecipitation of tungstate ions with ferric hydroxide. W = 1 mg; Fe = 0.1 mg-atom; $[NH_4Cl] = 1$ M; 1) 2 min; 2) 30 minutes - 2 hours; 3) 15-45 hours; 4) coprecipitation of 1 mg W with ferric hydroxide (0.2 mg-atom Fe); T = 30 min; I) 1-2 min. (Curve 1); II) 30 min; 100 µg W; III) 30 min; IV) 1 hr; V) 2 hr; VI) 15 hrs; VII) 22 hrs; VIII) 45 hrs; IX) 1 µg Re; 30 min.

Thus, bearing in mind Spitsyn's views on the formation of aquopolyanions, which depend to a considerable extent on a tendency to hydrogen bond formation on the part of the acid anions, which is characteristic for aquopolytungstates, one can postulate the following chemistry of the process for the increase in sorption of tungstate ions by ferric hydroxide with time; initially, the tungstate ions are sorbed by the surface of the hydroxide precipitate, sorption being realized by means of the hydrogen bond formed with the hydrogen atoms of the hydroxyl groups of the hydroxide. Subsequently, the sorbed tungstate ions can, at the expense of the water hydrogen ions which are necessary for forming new hydrogen bonds, combine with new tungstate anions, and this leads to an increase in sorption as a result of some polymerization (probably, di- or trimerization, since coprecipitation does not increase more than 2-3 times with the course of time) of tungstate ions on the surface of the hydroxide precipitate. Apparently, this process of polymerization on the precipitate surface occurs at higher pH values of the medium than in solution, as a result of the formation of a hydrogen bond between precipitate and anion. The presence of ammonium salts in solution gives rise to buffer properties in the medium. When a considerable amount of alkali is added to the solution, the tungsten sorbed by the precipitate goes into solution, which testifies to the surface character of the process.

On increasing the amount of carrier to 0.2 mg-atoms of iron, coprecipitation of tungstate ions, on precipitating ferric hydroxide in their presence, increases (Curve 4); the pH region within which complete coprecipitation of 1 mg of tungsten occurs increases to 8.6. Coprecipitation of perrhenate ions (1 μg Re) under the same conditions, in the presence of 1 mg of tungsten,hardly occurs at all, the behavior of the rhenium under these conditions is controlled by means of the radioactive isotope Re^{186}. This difference in the extent to which tungsten and rhenium are coprecipitated with ferric hydroxide in the pH range 5-8 can be used for the separation of these elements, the rhenium remains in solution, while the tungsten is completely precipitated.

SUMMARY

Tungstate ions are coprecipitated with ferric hydroxide quantitatively in the pH range covering the pH at which coagulation of the precipitate occurs, to pH 7.5-8.5; on increasing the pH further, coprecipitation decreases.

Coprecipitation of tungstate ions with ferric hydroxide is independent of ammonium chloride concentration, and increases with the time for which the precipitate is in contact with the solution.

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DETECTION OF SOME DIVALENT CATIONS BY MEANS OF β-HYDROXYNAPHTHALDEHYDE

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β-Hydroxynaphthaldehyde can be used for the quantitative determination of magnesium, copper, and beryllium [1-3]. Further studies have established that during the interaction of divalent cations with the aldehyde indicated in an alcoholic-aqueous-ammoniacal medium, imine compounds are not formed, but the complexes

$$(C_{11}H_7O_2)_2Me^{2+} \quad \text{or} \quad (C_{11}H_7O_2)_2Me^{2+} \cdot xH_2O \; [4].$$

are obtained.

The present article is devoted to the conditions necessary for obtaining characteristic crystalline precipitates of copper, beryllium, zinc, strontium, calcium, cobalt, and nickel ions with β-hydroxynaphthaldehyde, and to methods which have been developed for the qualitative detection of certain metals in mixtures and alloys.

Detection of Certain Cations. Copper. To 0.5 ml of the heated test solution is added 1 ml of a 2% alcoholic solution of β-hydroxynaphthaldehyde, two drops of 1 N sodium hydroxide is then added, light-yellow prismatic, needle-like – sometimes rhombic – crystals collected in sheafs immediately appear. The refractive index is 1.64; the crystals exhibit considerable pleochroism with strengthening of the yellow light. The limit of identification is 32 μg/ml; the limiting dilution is 1:32,000.

Beryllium. To 0.5 ml of test solution is added the same volume of a 2% solution of the aldehyde. The mixture is heated to the boil, and then one drop of 1 N sodium hydroxide is added; short, acicular, prismatic crystals are obtained, which sometimes have vertical shadings, they form characteristic ferny or branch-like aggregates colored a greenish-yellow color. The crystals belong to the hexagonal syngony and possess insignificant pleochroism with an increase in the greenish-yellow tone. The refractive index is 1.58-1.60. The limit of identification is 8 μg/ml; the limiting concentration is 1:128,000.

Other cations are detected like copper and beryllium.

Magnesium. From hot solutions, yellow, prismatic, pinacoidal, crystals separate out, and also acicular, star-like aggregates. The crystals possess a weak pleochromism of a yellowish color; the refractive index is 1.52-1.59. The limit of identification is 15 μg/ml; the limiting concentration is 1:64,000.

Calcium. Calcium separates out from cold solutions in the form of fine, light-yellow prisms with longitudinal shading. The crystals exhibit weak pleochroism with an increase or a decrease in the weak yellow color. The refractive index is 1.55-1.56. The limit of identification is 8 μg/ml; the limiting concentration is 1:128,000.

Strontium separates out almost immediately from cold solutions at a concentration of 1 mg/ml in the form of fine, long needles of a weak-yellow color collected into bundles. From more dilute solutions a precipitate settles out after 5 minutes. The pleochroism is weak with a small increase in the yellow color. The reaction has a low sensitivity.

Zinc, after adding to a hot mixture of equal volumes of a zinc salt and the aldehyde, two drops of 1 N sodium hydroxide, separates out in the form of weak greenish, columnar, acicular prism, which often collect in nodules. The pleochroism is weak with an increase in the yellow light, extinction angle 45°. The limit of detection is 32 μg/ml; the limiting concentration is 1 : 32,000.

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* Deceased.

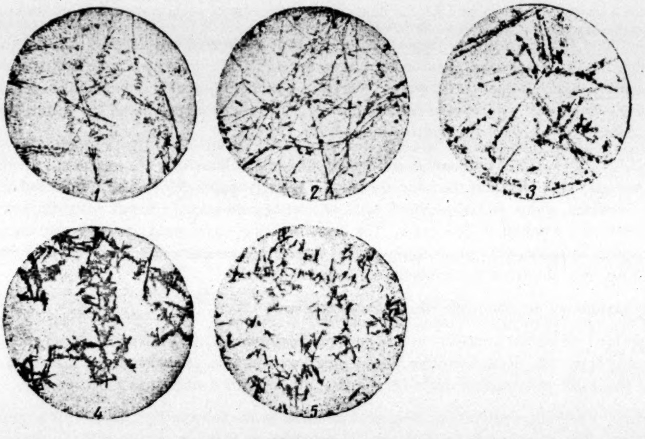
Manganese separates out from cold solutions after addition of β-hydroxynaphthaldehyde and one drop of 1 N sodium hydroxide. On shaking there are formed weak-yellow, fine, acicular crystals collected in ray-like and star-like formations. The pleochroism is weak and yellow in color. The refractive index is 1.65. The limit of identification is 32 μg/ml; the limiting concentration is 1 : 32,000.

Cobalt and Nickel give, from hot solutions, on addition of the aldehyde and one drop of sodium hydroxide, almost identical greenish-yellow, prismatic crystals, gathered in star-like and radial ray-like aggregates. The pleochroism is weak with an increase in the lemon-yellow color. The refractive index is 1.58-1.60. The limit of identification is 16 μg/ml; the limiting dilution is 1 : 64,000.

Analysis of Mixtures of Certain Cations. Magnesium and calcium can be detected in the presence of strontium in weakly alkaline solutions. In the cold there are formed crystals of the compounds of β-hydroxynaphthaldehyde with calcium and magnesium cations which can be distinguished by differences in their form.

The limiting ratios are as follows: Sr : Ca = 6 : 1 (Fig. 1); Sr : Mg = 2.6 : 1 (Fig. 2).

Beryllium can also be detected in the presence of copper on the basis of the formation of crystals which are characteristic for each of them taken separately. The limiting ratio is Cu : Be = 5 : 1 (Fig. 3).



Figs. 1-5.

Detection of Beryllium in Bronze and Steels. 0.25 g of bronze containing about 2% beryllium is dissolved on heating in 5 ml of 1 N nitric acid, the solution is then diluted with water to 100 ml. To 1 ml of this solution, which contains about 0.05 mg Be/ml, is added four drops of a 10% solution of sodium ethylenediaminetetracetate until a blue color appears, 1.5 ml of a 2% alcoholic solution of the aldehyde is then added, and, after heating, a few drops (about 4) of 1 N sodium hydroxide is added until an emerald-green color appears. On shaking, a precipitate of the beryllium compound separates out (Fig. 4). The minimum beryllium concentration that can be detected is 25 μg/ml. Beryllium can be detected in the same way in steels (Fig. 5).

SUMMARY

Crystalloscopic methods have been developed for the detection of Ca^{2+}, Be^{2+}, Mg^{2+}, Sr^{2+}, Zn^{2+} and other divalent metals by means of β-hydroxynaphthaldehyde in an alcoholic-alkaline medium. Crystalline precipitates are obtained at pH 7.5-8.

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MICRODETERMINATION OF COPPER IN ORGANIC COMPOUNDS BY COMBUSTION IN OXYGEN

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In recent years the attention of analysts has been drawn to Schoniger's method which permits determination of a number of elements in nonvolatile organic compounds. An aliquot of test material is wrapped up in filter paper, the latter is wound with platinum wire, and the paper is burnt in a flask filled with oxygen. The method has been successfully used for the determination of halogens [1], sulfur [2], and phosphorus [3]. It is obvious that it could also be used for the analysis of the organic complex compounds of a number of metals. In this article we shall describe a technique for the analysis of inner complex compounds of copper.

An aliquot of test material containing 4-5 mg is weighed out on a microbalance, in a glass tube with a long tip, and it is strewn onto the middle of an ashless filter paper. The filter is folded up in such a fashion as to leave a free end, and is fitted to the end of a platinum wire fused into a flask as indicated in Schoniger's method [1, 2].

Twenty ml of 0.5 N sulfuric acid is poured into a 500 ml conical flask and oxygen passed into the flask for several seconds from a cylinder. The free end of the filter paper is ignited and is immediately introduced into the flask, the stopper is held in position in the flask by hand for the first few seconds otherwise it will be blown out. Combustion is complete in a few seconds. The flask is then shaken and a few drops of water introduced along the glass stopper into the flask which is then allowed to stand for 15-20 minutes. The tap is opened and the stopper removed and rinsed with water. The solution is transfered from the flask into a 100 ml conical flask and is heated to the boil. The platinum wire is heated for several seconds in the oxidizing flame of a burner in order to oxidize any small amounts of metallic copper which may have been formed, the wire is then lowered into the flask containing the solution and the latter boiled for 1-2 minutes. When all the cupric oxide has dissolved, the wire is rinsed with water, and the solution evaporated to a volume of 15 ml.

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* Original Russian pagination. See C. B. translation.

To the cooled solution is added 25% ammonia until a weak blue color appears, 5 ml of 50% acetic acid solution is then added followed by about 1 g of potassium iodide; the liberated iodine is titrated with 0.02 N sodium thiosulfate until a weak yellow color is obtained, 1 ml of a 1% starch solution is added and titration continued until the color changes from blue-brown to white-rose.

The experimental error is ± 0.2%. A determination takes about 30 minutes. Results of some determinations are given in the table.

Test material	Sample wt.	Copper content, %		
		found	calc.	difference
Copper salicylal	23.091	20.83	20.73	+0.10
$C_{14}H_{10}O_4Cu$	22.919	20.61		−0.18
Copper salicylalmethylamine	24.259	19.35	19.15	+0.20
$C_{16}H_{16}O_2N_2Cu$	24.919	19.28		+0.13
Copper salicylalimine	27.438	21.00	20.90	+0.10
$C_{14}H_{12}O_2N_2Cu$	27.010	20.88		−0.02
Cu salt of β-hydroxynaphthaldehyde	23.832	15.63	15.65	−0.02
$C_{22}H_{14}O_4Cu$	23.450	15.77		+0.12
Cu salt of benzoylacetone	14.537	16.44	16.37	+0.07
$C_{20}H_{20}O_4Cu$	18.114	16.32		−0.04
Copper salt of benzoylacetaldehyde	19.253	17.65	17.78	−0.13
$C_{18}H_{14}O_4Cu$	17.388	17.85		+0.07

SUMMARY

A rapid method has been developed for the determination of copper in organic compounds, it is based on combustion in a flask filled with oxygen, with subsequent iodometric titration of the copper. The error is ± 0.2%.

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SPECTROPHOTOMETRIC TITRATION OF ERBIUM WITH SODIUM ETHYLENEDIAMINETETRACETATE (EDTA-Na) IN THE PRESENCE OF PYRIDYL-(2-AZO-4)-RESORCINOL

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The rare earths form colored complex compounds with pyridyl-(2-azo-4)-resorcinol (PAR) in neutral or weakly alkaline media. In Fig. 1 are shown absorption curves of the complex compound of erbium with PAR (Curve 1), and of a solution of the indicator itself (Curve 2). They show that it should be possible to titrate erbium spectrophotometrically using PAR as an indicator at the absorption maximum of 504 mμ. Titration at the absorption maximum of the indicator at 415 mμ is impossible because of the appreciable absorption of the compound of erbium with PAR. Sodium ethylenediaminetetracetate (EDTA-Na) was used as the titrant. It is clear from Fig. 2 that maximum absorption of solutions of the compound of erbium with PAR occurs at pH 8.0-8.8.

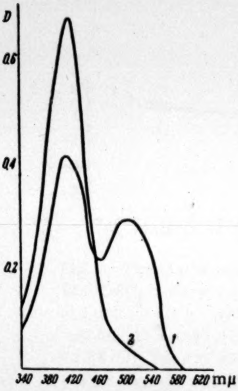

Fig. 1. Absorption curves: 1) 1×10^{-3} M solution of the compound of erbium with pyridyl-(2-azo-4)-resorcinol; 2) 2×10^{-3} M solution of pyridyl-(2-azo-4)-resorcinol; pH 8.5.

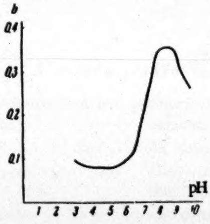

Fig. 2. The relation between the optical density of solutions of the compound of erbium with pyridyl-(2-azo-4)-resorcinol and pH.

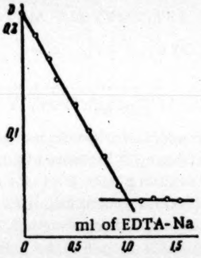

Fig. 3. Titration of an erbium salt with EDTA-Na in the presence of pyridyl-(2-azo-4)-resorcinol.

Spectrophotometric titration of erbium with EDTA-Na solution using PAR as indicator is carried out at 504 mμ and a pH of 8.5, using a SF-4 instrument and a cuvette of optical glass with a capacity of 25 ml. The EDTA-Na solution is added from a 2 ml microburet, and is stirred with a glass stirrer, for this purpose the metal lid of the spectrophotometer is replaced by a bakelite lid with two holes.

For titration, to the cuvette containing 10 ml of an acetate-ammoniacal buffer with pH 8.5 is added 0.3 ml of a 2×10^{-3} M aqueous solution of PAR, various amounts of erbium, and the solution diluted to 20 ml. The end point on titrating with a 5×10^{-3} M solution of EDTA-Na is determined by the intersection point of two straight lines (Fig. 3).

Results of titration of erbium with EDTA-Na in the presence of PAR (Table) confirm the possibility of determining total rare earths (on the basis of erbium titration) by indicator spectrophotometric titration, with an error which does not exceed the limits of the possibility of this method. The possibility of determining the rare earths with PAR is determined by the high sensitivity of the reaction with the indicated reagent (for erbium the sensitivity of the reaction is 0.2 $\mu g/ml$; the molar absorption coefficient $\epsilon = 46{,}000$). The method permits determination of 10^{-4} - 10^{-3} g of the rare earth element.

There is a possibility that the rare earths can be determined in the presence of thorium at pH 8.5.

Er taken, mg	Amt. of EDTA-Na solution used, ml	Er found, mg	Error	
			mg	%
0.334	0.39	0.326	—0.008	—2.4
0.502	0.64	0.535	+0.033	+6.6
0.836	0.98	0.819	—0.017	—2.0
0.836	0.98	0.819	—0.017	—2.0

SUMMARY

A method has been developed which is suitable for the determination of 10^{-3} to 10^{-4} g of erbium and the total rare earths. The experimental error is 3-4%.

A NEW TITRIMETRIC METHOD OF DETERMINING RHENIUM IN ALLOYS

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Titrimetric methods of determining rhenium are not numerous. The method of reducing septivalent rhenium with zinc, followed by titration with solutions of oxidizing agents [1, 2], have not found practical application because of the poor reproducibility of the results obtained. Reduction of perrhenate by a bismuth amalgam has been used by Lazarev [3] for the quantitative determination of rhenium in solutions free from foreign impurities. We have developed a titrimetric method for the determination of rhenium which is based on the quantitative reduction of septivalent rhenium to the quadrivalent state by means of a standard solution of a divalent chromium salt [4].

In trying to find the effect of small amounts of molybdenum on the determination of rhenium by the method of chromometric titration [4], the optimum conditions were established (acidity, temperature). When the amount of molybdenum present is a few times greater than the amount of rhenium, most of the molybdenum should be removed by an extraction method [5-12], chromatographically [13-14], or by distillation [15]. Iron,* titanium, chromium, vanadium, niobium, copper, and manganese can be readily removed by precipitating them with ammonia or alkali.

As a result of our work we have developed a technique for the determination of rhenium in alloys of varying composition (Table).

Composition of the alloy	Rhenium found, %		
	by thiocyanate method and by spectrophotometric meas. of perrhenate in alkaline region	by titration with $CrSO_4$	
		parallel determinations	Mean
Re, Ni (77.0), Mn (0.5), Fe (21.0)	1.0	0.96; 0.99	1.0
Re, Mo (0.57), Ni (69.0), Mn (0.5), Cu (28.0), Ti (2.0)	1.5	1.51; 1.51	1.5
Re, Co (51.0), Fe (38.0)*	10.40	10.00; 10.24	10.1
Re, Co (51.0), Fe (42.0)	5.90	6.17	6.2
Re, Fe	3.0	2.98	3.0
Re, Cr, Al, Ni	3.5	3.38; 3.48	3.4
Re, Cr, Al, Fe	11.0	10.90	10.9
Re, Ti, Ni, Fe	2.5	2.32; 2.32; 2.53	2.4
Re, Ni	7.10	7.04	7.0
Re, Cr, (20.0), Fe (70.0), Al, V (3.3)	not determined	1.56; 1.63; 1.45	1.5
Re, Mo (0.3), Cr, Fe, V	Ditto	0.98; 0.88	0.9
Re, Mo (5.5), Ni, Cr, Fe**		13.45; 13.40; 12.95	13.3

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* The titration curve is shown in Fig. 1.

** The titration curve is shown in Fig. 2.

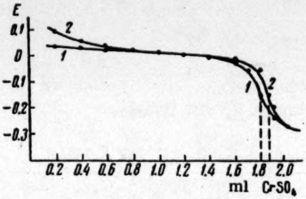

Fig. 1. Titration of septivalent rhenium with $CrSO_4$ in alloys containing cobalt and iron. 0.510 g of alloy; total V = = 50 ml; 1) 0.0895 N $CrSO_4$; V_{CrSO_4} = = 1.80 ml; V_{Re} = 10 ml; Found 10.00% Re; 2) V_{Re} = 10 ml; 0.0885 N $CrSO_4$; V_{CrSO_4} = 1.86 ml; Found 10.24% Re.

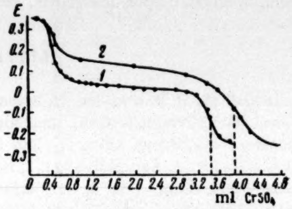

Fig. 2. Titration of septivalent rhenium with $CrSO_4$ in alloys containing Ni, Cr, Fe, and Mo (5.5%). 1) 0.5009 g of alloy; total V = 50 ml; 0.0720 N $CrSO_4$; $2V_{Re}$ = 10 ml; V_{CrSO_4} = 3.44-0.44 = = 3.00 ml; Found 13.40% Re; 2) 0.05005 g of alloy; total V = 50 ml; 0.0634 N $CrSO_4$; V_{Re} = 10 ml $CrSO_4$ = 3.90-0.48 ml = 3.42 ml; found 13.45%.

Reagents and Apparatus. A solution of a divalent chromium salt was prepared by A. I. Busev's method [16], while its concentration was determined by titration with $CuSO_4$ in HCl 1 : 1 [17]. The $CuSO_4$ was standardized electrolytically. Titration with the $CrSO_4$ solution was carried out in a small thermostatted cell [18] in an atmosphere of purified nitrogen. The potentials were measured by a compensation method on a Leeds and Northrup potentiometer. The indicator electrode was a platinum disc 0.2 × 1 cm, fused into a glass tube. The reference electrode was a saturated calomel electrode.

Titration Procedure. 0.5 g of alloy is dissolved in a mixture of hydrochloric and nitric acids (5 ml of concentrated HNO_3 + 5 ml of concentrated HCl) on heating. After the alloys had dissolved completely, the solution is evaporated on a water bath. To the 2-3 ml of residue is added a small amount of water and 2 ml of concentrated H_2SO_4, and the evaporation repeated on a water bath. In order to remove nitric acid completely the evaporation is completed on a moderate hot plate until thick white fumes of SO_3 appear. By observing this condition there is almost no loss of rhenium.

The salt residue is dissolved on heating in 50 ml of water; the usual operation of precipitation with ammonia (for alloys containing Cr, V, Ti, and Fe) or alkali (for alloys containing Co, Ni, and Cu) [19] is then carried out from a hot 5% solution. The filtrates are evaporated to a small volume, and acid is added until the solution gives a neutral reaction with litmus paper; concentrated H_2SO_4 is finally added until its concentration in the solution is 5-6 N (7 ml of concentrated H_2SO_4 for 50 ml of the final volume).

Aliquots of 5, 10, or 20 ml of the solution are taken for titration, the amount taken being dependent on the rhenium content. The solution is placed in a special titration cell [18] through which is passed a stream of purified nitrogen. The cell is heated to 80° by means of a thermostat. KI crystals (about 1 mg) are added as a catalyst for the reduction of rhenium. The $CrSO_4$ solution is added from a 10 ml microburet. The potential of the platinum indicator electrode is measured on the potentiometer (as the potential jump approaches, the solution should be added dropwise).

When molybdenum is present, titration is carried out to the second potential jump on the platinum indicator electrode. The difference in the volumes of $CrSO_4$ solution used between the second and first potential jumps corresponds to the amount of $CrSO_4$ used for titrating the rhenium.

SUMMARY

A titrimetric method has been developed for the determination of rhenium; it is based on quantitative reduction of Re^{VII} to Re^{IV} by means of a solution of a divalent chromium salt, the titration end point being controlled potentiometrically. The method has been checked on alloys containing nickel, cobalt, chromium, iron, vanadium, titanium, copper, manganese, and molybdenum.

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* Original Russian pagination. See C. B. translation.

MICROCRYSTALLOSCOPIC DETECTION OF SULFUR-CONTAINING ANIONS

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There are no satisfactory methods for the microcrystalloscopic detection of the anions SO_4^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$ [1, 2]. The tetrathiourea salt of platinum $[Pt(SCN_2H_4)_4]Cl_2$,* obtained by Kurnakov [3] can be successfully used for detecting these anions.

This compound forms sparingly soluble characteristic crystals with the anions indicated.

The SO_4^{2-} ion, independently of the cation, gives $[Pt(SCN_2H_4)_4]SO_4$. The sulfate ion cannot penetrate into the inner sphere of the complex.

On mixing drops of the test solution containing SO_4^{2-} ions with a drop of the reagent solution, crystals are formed in the form of characteristic crosses (Fig. 1). Crystals in the form of fern leaves collected in the

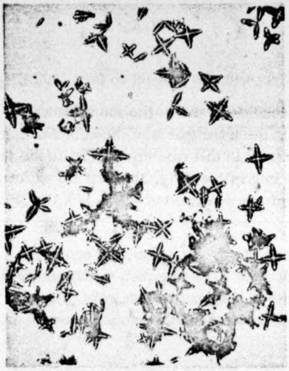

Fig. 1

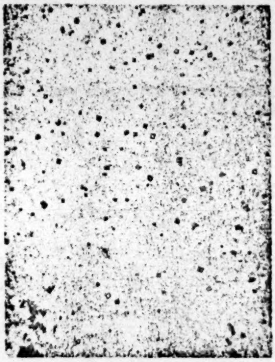

Fig. 2

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* A compound with this composition can be readily prepared from potassium chloroplatinite and thiourea. In order that the salt obtained be free from foreign impurities it is best to prepare it in two stages. First of all, solutions of potassium chloroplatinite and thiourea are mixed in the molar ratio of 1 : 2 at room temperature. Platinum dichlorodithiourea $[Pt(SCN_2H_4)_2Cl_2]$ is precipitated. The precipitate is filtered off and washed free from potassium chloride. To one mole of the precipitate separated in this way is then added a further two moles of thiourea at 50-70°. During this stage the precipitate dissolves to form $[Pt(SCN_2H_4)_4]Cl_2$.

On careful evaporation there separates out a crystalline material which is bright-yellow in color and which is readily soluble in water. The salt obtained is used for microcrystalloscopic detection in the form of an aqueous solution whose concentration is 10-15 mg/ml.

form of a cross are obtained when the concentration of sulfate ions is high enough (up to 0.02 M). In the case of comparatively dilute solutions containing sulfate ions, square plates with a cross along the diagonals (Fig. 2) can be seen under the microscope. These crystals, under higher magnification prove to be the same sort of crystals as in the first instance but are not so developed. The limiting SO_4^{2-} concentration is 0.0002 M.

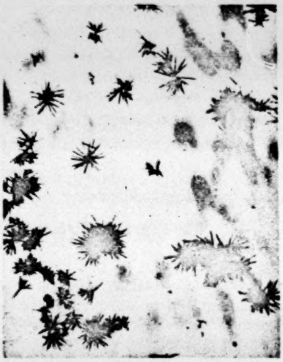

Fig. 3

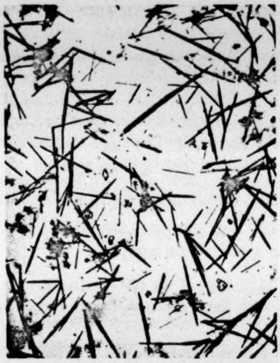

Fig. 4

Sulfite ions interact with the reagent to form $[Pt(SCN_2H_4)_3SO_3]$.

Under ordinary conditions, the sulfite ion replaces only one molecule of thiourea in the inner sphere of the complex compound [4]. The compound formed in this case crystallizes in the form of fine needles collected into spheres (Fig. 3) which are yellowish in color. The reaction permits detection of SO_3^{2-} ions in 0.002 M solutions.

During the interaction of $S_2O_3^{2-}$ ions, the compound $[Pt(SCN_2H_4)_3S_2O_3]$ is formed. The platinum is connected with the sulfite ion through sulfur in the quadrivalent state, while the platinum is connected with the thiosulfate ion through the external atom of divalent sulfur.

A sparingly soluble compound in the form of long prisms, yellow in color, is formed with $S_2O_3^{2-}$ ions.

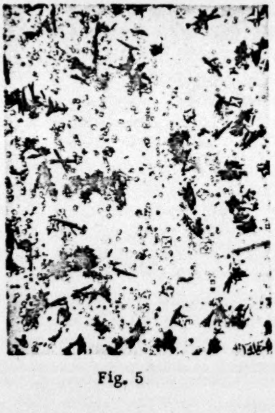

Fig. 5

Further substitution of thiourea molecules in the inner sphere of the complex by $S_2O_3^{2-}$ ions may occur, with formation of two compounds containing a greater number of thiosulfate residues in their composition [5]. Accordingly, high concentrations of the thiosulfate solutions must be avoided (0.05-0.001 M with respect to thiosulfate). At higher thiosulfate concentrations a bright-yellow crystalline precipitate separates out (Fig. 5).

On adding a solution containing a mixture of SO_4^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$ to a solution of the reagent, it is possible to detect all three ions. It is possible to detect relatively small amounts of SO_3^{2-} and $S_2O_3^{2-}$ ions in the presence of large amounts of SO_4^{2-} ions.

SUMMARY

The reagent $[Pt(SCN_2H_4)H_4]Cl_2$ forms sparingly soluble salts with characteristic crystalline forms with SO_3^{2-}, $S_2O_3^{2-}$, and SO_4^{2-} ions. This reaction permits the detection of these ions even when they are present together.

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